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Water Management in a PEM Fuel Cell using two phase single-domain Model

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Abstract

In the present work, we have developed a mathematical model for liquid water formation and its transport in all regions of PEM fuel cell. The governing equations are presented for water both in vapor and liquid at equilibrium and when it is present individually. Using appropriate assumptions together with CFD technique leads to a single domain numerical solution. The governing equations are solved and theoretical performance of a PEM fuel cell is investigated by looking at parameters such as pressure, temperature, water in liquid and vapor form and species concentration in two-phase region. The results are shown to be in good agreement with previous work and it is validated with recent experimental data available.

Introduction

Low operating temperature and zero or low emissions have made PEM fuel cells as the most promising power source for vehicle and in portable applications. However, for commercialization the performance of PEM fuel cells has to be improved further. Water management is critical parameter in overall cell performance. Water management in PEM fuel cells involves balancing of operations to avoid flooding while maintaining membrane hydration. The membrane in PEM fuel cell must be fully hydrated to gain high proton conductivity. However, when too much water accumulates in the cathode, it condenses and blocks some of the pores, reducing oxygen transport, resulting flooding in the cathode side of the PEM fuel cell[1]. Two-phase transport of reactants and products constitutes a limiting factor of PEM fuel cell performance, and the behavior of gas liquid two-phase transport is very important in understanding of fuel cell operation. A comprehensive numerical model is a useful tool for understanding and describing the two-phase processes and water management in a cell. Many models with various capabilities have been presented for water management and predicting PEM fuel cell performance [2-6]. Some of these models are isothermal, in which the effect of temperature variation on phase change has not been considered. Also, in some other cases either particular regions of fuel cell have been modeled or they had to use boundary condition in the interfaces of layers when the model is not single-domain.

In this work a two phases, single-domain, non-isothermal, with coupled electrochemical and unsaturated reactant gas streams is modeled in PEM fuel cell to develop a detailed cell performance and thermal model incorporating water and temperature distribution in the cell, and to investigate the operating conditions and cell performance as well as water distribution.

Governing Equations and Numerical Procedures

In this model, the computational domain consists of five-layer membrane-electrode assembly. These are two gas diffusion layers, two catalyst layers, and a polymer electrolyte membrane. Humidified hydrogen and saturated air enters through anodic and the cathodic gas channels, respectively. In the anodic catalyst layer, hydrogen is consumed to form protons and electrons where the protons are carried by ionic current to the cathode. However the electron passes through the conductive diffusion layer and in external circuit that finally produces electric work. In the cathodic catalyst layer, the electrochemical reaction not only consumes the oxygen but also results in water.

The cell is considered to be one-dimensional and steady state. The other assumptions used in this model are: the reactant gas mixtures are assumed to be ideal gases, the gas flow is laminar and incompressible, the membrane is considered impermeable to gases, the cathode catalyst layer is uniform and fully hydrated and the gas diffusion layer is isotropic, homogenous, and does not extend into the gas channels. The governing equations include conservation of mass, momentum, ionic charge, and energy for each individual species.

$$\nabla.(\rho\vec{u}) = 0 \qquad \text{Mass (1)}$$

$$\frac{1}{\varepsilon^2}\nabla.(\rho\vec{u}\vec{u}) = -\nabla p + \nabla.(\mu\nabla\vec{u}) + S_{Dar} \qquad \text{Momentum (2)}$$

$$\nabla(\gamma_C^i\vec{u}C^i) = \nabla\left[\varepsilon D_g^{i,eff}(1-s)\nabla C_g^i\right] - \nabla\left[(\frac{mf_l^i}{M^i} - \frac{C_g^i}{\rho_g})\vec{j}_l\right] + S_k \qquad \text{Species (3)}$$

$$\nabla.(\sigma_m\nabla\varphi_m) = S_{pc} \qquad \text{Charge (4)}$$

$$\nabla.(\gamma_h\rho C_p\vec{u}T) = \nabla.(k^{eff}\nabla T) + S_T + h_{fg}\dot{m}_{fg} \qquad \text{Energy (5)}$$

The governing equations are discretized using a finite volume method and solved by a computational fluid dynamic code. The pressure and velocity fields are treated with the SIMPLER pressure correction algorithm.

Results and Discussion

Model validation is carried out using numerical and experimental results in literature. Fig.1 shows the water flux across the membrane as a function of the local current density where relative humidity is 100% in the anode gas stream. At low current densities, the water flux is negative. Because water is transported from the cathode to the anode due to back diffusion arising from the water concentration gradient, but at high current densities it becomes positive, signifying the dominant effect of electro-osmotic drag of water transport. Also by considering the same curve in the cathode catalyst layer, the influence of electro-osmotic drag is readily apparent. At low current density, there is very little change in water content across the membrane electrode assembly. This is due to a relatively low amount of drag and the fact that vapor activity at anode and cathode is almost identical. At high current density, the water content curve becomes steeper as the anode dehydrates and the cathode water content increases. An interesting ability of this model is to Predict the water flux through gas diffusion layers. Where, saturation is not assumed and interaction of liquid water flux and water vapor flux in the GDLs could be investigated. As it is expected the vaporization or condensation of water is very low in fully humidified stream conditions.

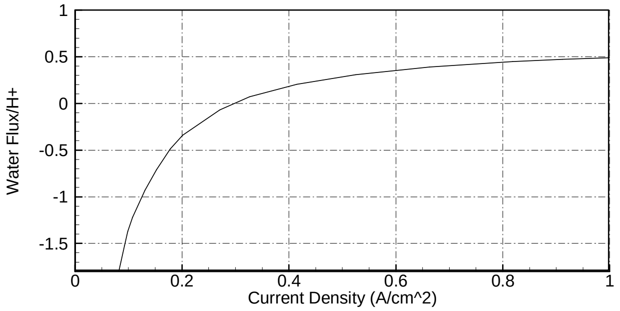

Fig. 1. Net water flux across the membrane

In operation with a partially hydrated membrane and catalyst layers as well as back diffusion of water from the cathode to the anode, the net amount of water moved per proton is well predicted by this model that is between 0.17 and 0.35. The water transported across the MEA, from the anode to the cathode, makes up between 20 and 40% of the total amount of water accumulation at the cathode. This indicates that in addition to limiting cell performance by means of anode dehydration, water transport by electro-osmotic drag is the cause of significant fraction of the liquid water buildup at the cathode and limiting the reactant transport.

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High temperature proton exchange membrane fuel cells: Advantages and technical challenges

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Abstract

High temperature proton exchange membrane fuel cells (HT-PEMFC) have attracted great interests in recent years due to their advantages compared with common PEMFC. PEM fuel cells based on perfluorinated membrane electrolytes operate in the temperature range between 60 and 80°C while elevating the operating temperature (up to 200°C) provide improved carbon monoxide tolerance, faster electrode kinetics, simpler thermal and water management and more efficient recovery of waste heat as a practical energy source. In this investigation the drivers behind the interest in HT-PEMFCs and the challenges in developing novel materials for membranes preparation is reviewed. Also a brief analysis of temperature requirements for CO tolerance is presented. The research shows an exhaustive presentation and comparative discussions on various types of high temperature membranes. Finally, the importance of porosity in electrodes for HT-PEM has been studied.

Keywords: HT-PEM fuel cell; Polymer electrolyte; PBI; NafionTM

Introduction

Fuel cells, due to their special characteristics, are making a great progress in power generation. Polymeric fuel cells have several advantages compared with other ones. These advantages include high power density, high efficiency, rapid startup and low corrosive effects. Furthermore, existence of solid electrolyte eliminates leakage of materials in these kinds of fuel cells [1]. Common polymeric fuel cells cannot operate at temperatures above 80°C, because at higher temperatures, membrane structure would be denatured and proton conductivity of the membrane will be decreased [2]. HT-PEM is a kind of polymeric fuel cells that can operate at higher temperatures (120 – 200 °C).

Advantages of HT-PEM

- Higher CO tolerance in feed gas: CO poisons Pt catalyst by an exothermic reaction. So by increasing temperature, adsorption of CO on Pt would be decreased and feed gas can contain higher concentrations of CO [3].
- Faster reaction, especially at the cathode site: The overall electrochemical kinetics of PEM is determined by oxygen reduction reaction. By increasing temperature the amount of current exchange density increases and the activation over potential decreases [4].
- Improved heat management: By increasing the temperature difference between fuel cell stack and ambient, the required area for heat transfer would be decreased. Furthermore, under high temperatures, the heat can be recovered as, e.g. steam , which in turn can be used for direct heating and steam reforming[4,5].
- Improved water management: At high temperatures, water is in the vapor state and the flooding does not happen.
- Simpler humidification system: The membranes used in HT-PEM are fewer dependants on humidity for proton conducting. Therefore the system used for humidifying inlet gases can either be eliminated or simplified.

High temperature fuel cell challenges

At high temperatures, humidity of common membranes decreases and this will have negative effect of the proton conductivity. This has interested researchers to investigate on new proton exchange membranes. Their investigations can be grouped in two fields:

- Modification of common membranes such as NafionTM, by adding hydrophilic materials for operation at high temperatures [6-8].

Preparation of new high temperature membranes. These membranes don’t require water media for proton conduction [9, 10].

The results show that the membranes of second group have better performance than the first ones. This happens because proton conductivity in water media is restricted by increasing temperature.

Conclusion

Because of elimination of humidification system, decrees in heat transfer area and H_2 purity in the feed gas, HT-PEMFC has lower costs compared to common PEM. Also by comparing different researches, it is found that among different membranes, polybenzymidazole (PBI) has the best performances at high temperature conditions. However PBI is the only membrane for which proton conduction increases by increasing temperature [10, 11]. On the other hand PBI has been commercialized due to its low cost of preparation.

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METHANOL PERMEABILITY OF NAFION/FUNCTIONALIZED ZEOLITE-A COMPOSITE MEMBRANE FOR DIRECT METHANOL FUEL CELL

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Abstract

Composite membrane made of zeolite HA and Nafion 117 is formed by solution casting method. The external surface of zeolite HA has been functionalized in order to improve the interface bonding between Nafion ionomer and zeolite crystals. By incorporating functionalized zeolite HA, methanol permeability of composite membrane is reduced as much as 69%. The effect of temperature on methanol permeability is discussed.

Keywords: membrane, Nafion, zeolite A, DMFC, methanol permeability

Introduction

Fuel cells are classified into five major types according their temperature range, pressure and their type of electrolyte. Among them DMFC's, direct methanol fuel cells, have gained more interest because of their simplicity and compact design. But one major drawback of DMFC's is that methanol crossover through membrane from anode to cathode causes mixed potential which in turn decreases the fuel cell efficiency. The chemical Nafion falls into the category of PFSA's (perflurosulfonic acid) and is uniquely produced by DuPont Chemical plant. It has a high methanol cross over whereby considerable fuel is wasted. But mechanical and chemical stability due to C-F bonds put this disadvantage out of focus and makes it a commercial ionomer extensively used in DMFC's [1]. But, this problem can be largely overcome by using such inorganic compounds as zeolite. Zeolite A has

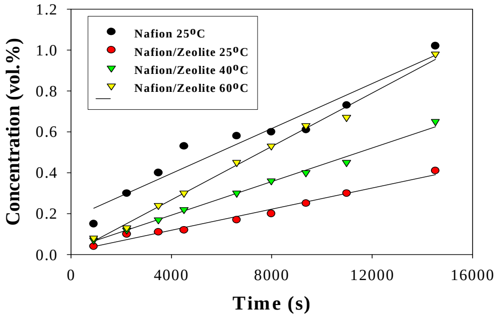
Si/Al = 1 which gives it a hydrophilic character, that selectively adsorbs water over methanol molecules in its channels. In the present work we describe the preparation of functionalized zeolite HA/Nafion membrane and also investigate methanol permeability.

Experimental

Nano size zeolite NaA with particle size of 80 nm is converted into H^+ form. Surface of zeolite HA is functionalized using 3-aminopropyltrimethoxysilane (APTS), to achieve good cross linking between zeolite and Nafion. Nafion and Nafion/zeolite HA composite membrane were fabricated via solution casting method [2]. Effect of temperature in methanol permeability of Nafion/Zeolite HA composite membrane is evaluated using diffusion cell and gas chromatography technique [3].

Result and discussion

The data shows that incorporation of functionalized zeolite HA leads to a significant decrease in methanol permeability; this is attributed to a better adhesion between zeolite A and Nafion that prevent formation of pinholes in mix matrix membrane. Nano size zeolite HA has larger outside surface area than the micron size type. As a result more contact with polymer matrix and much more homogenous distribution of zeolite A into polymer matrix can be achieved. The concentration values are used in determining the methanol crossover flux and permeability of the membrane. Concentration in receiving cell is increased with temperature, as shown in Figure 1. Fig.2.a,b show an increase in the permeability of the membrane in the temperature range 25ºC-60ºC according to an Arrhenius-type function. Fig.3. shows Arrhenius plot of permeability as a function of temperature for Nafion/Zeolite HA membrane. Figure 4 shows an increase in flux value with an increase in temperature. This is due to increase in the concentration gradient during the crossover of methanol through the membrane.



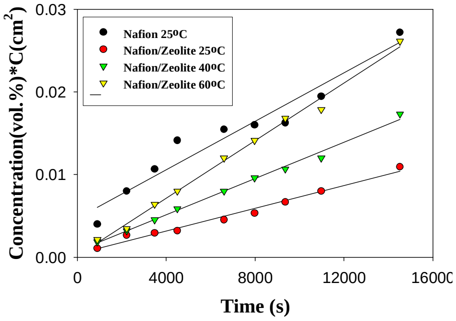
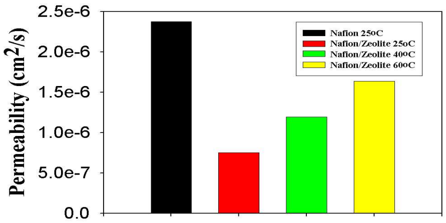


Fig. 1. Concentration Vs. time of methanol permeate Through Nafion membrane at 25ºC and Nafion/Zeolite HA membrane at 25°C, 40°C, 60°C

Fig.2.a Methanol permeability of Nafion membrane and Nafion/Zeolite HA membrane at 25°C,40°C,60°C where C is(Vb*l/Ca*A)



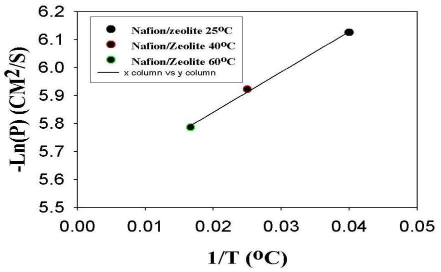
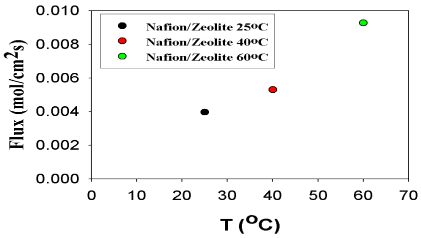


Fig.2.b Methanol permeability of Nafion membrane As a function of temperature for Nafion/Zeolite HA membrane

Fig.3. Arrhenius plot of methanol permeability and Nafion/Zelite HA membrane at 25ºC, 40ºC, 60ºC



membrane	***flux(mol/cm^{2}s)***
Nafion 25 ºC	0.00663
Nafion/zeolite25 ºC	0.00397
Nafion/zeolite40 ºC	0.00529
Nafion/zeolite60 ºC	0.00927

Fig. 4. Methanol crossover flux for Nafion membrane at 25ºC and Nafion/Zeolite HA membrane at 25ºC, 40ºC, 60ºC.

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The hydrogen effect on the oxygen reduction reaction on the Ag deposited on graphite in aqueous and non aqueous bath.

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Abstract

Oxygen reduction reaction in alkaline electrolytes has been of great interest for decades due to its importance for alkaline fuel cell and brine electrolyzer. Finding a catalyst with good performance to this reaction and low cost is one of the most aims of researches that have been carried out in this field.

Silver has been one of the famous catalysts for ORR at alkaline media for high catalytic activity to peroxide decomposition from many years ago. Silver has been used as Ag/C or alloying with other metal [1-3]. At almost of the researches that have carried out with Ag/C, this catalyst prepared by dispersion of silver on carbon however, deposition method has been used recently by some author [4].The effect of hydrogen on ORR has been reported only as the effect of hydrogenation of adsorbed oxygen on Cu and Ni.

In this research, the effect of hydrogen on the ORR on three electrodes: graphite (EK20), (Ag/EK20)$_{aq}$ and(Ag/EK20)$_{naq}$ have been studies in alkaline media by cyclic voltammetery, EIS and chronopotentiometery. The reduction and oxidation peaks of oxygen and hydrogen have been distinguished. The negative effect of atomic hydrogen on reduction of oxygen has been discussed. According to our result, at research condition the optimized time for electro deposition for (Ag/EK20)$_{aq}$ and(Ag/EK20)$_{naq}$ is 50 second. The diffusion coefficient of oxygen was calculated and it is equal to1.55×10^{-5} Cm^{2} s^{-1}. To avoid of hydrogen effect, the electro deposition carried out in nonaqueous solution. The catalytic effect of this electrode improved and show better response to oxygen reduction (fig1) because of different crystal structure and the absence of atomic hydrogen. Furthermore, the reduction of H$_{UPD}$ during experiments has negative effect

on the electrochemical behavior of $(Ag/EK20)_{naq}$.

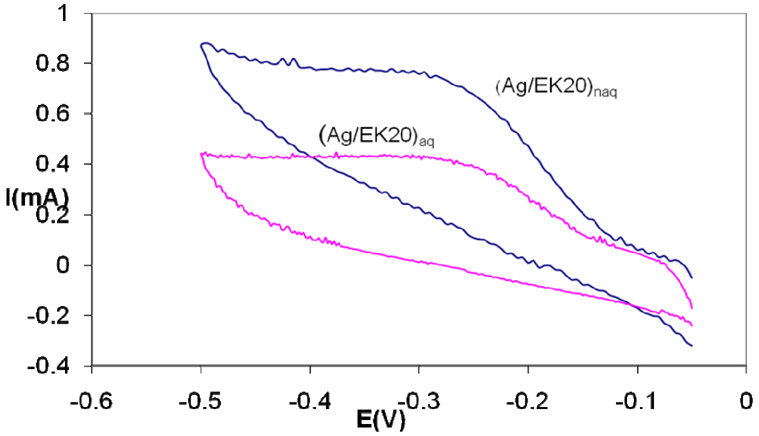

Fig1. Comparison between response of $(Ag/EK20)_{aq}$ and $(Ag/EK20)_{naq}$ to oxygen reduction, scan rate: $100mVs^{-1}$

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Electrochemical oxidation of saccharose at copper electrode in alkaline media

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1. Introduction

In spite of comprehensive investigations have been carried out during the past several decades on the electrocatalytic oxidation of alcohols, poly-alcohols and carbohydrates at different catalytic metal electrodes for the sake of the development of analytical sensors and fuel cells [1,2], a few of them directly oriented towards saccharose (sucrose, $C_{12}H_{22}O_{11}$) electro-oxidation as a carbohydrate compound.

Various authors have shown that carbohydrates can be oxidized directly at a variety of electrode materials, including metals such as platinum [3, 4], gold [4, 5], copper [4, 6-8], indium [4], rhodium [4], or metallic complexes such as cobalt phthalocyanine [9]. In this research work, the use of metallic copper as an electrode has been studied for some reasons. Although considerable currents were observed at it, it is too cheap to afford practical applications.

2. Experimental

A copper disk electrode was used both stationary electrode and rotating disk electrode. A Graphite rod and a homemade Ag/AgCl, were employed as counter and reference electrodes, respectively. The electrochemical experiments were carried out in a conventional three electrode cell powered by a potentiostat/galvanostat (BHP 2061-C Electrochemical Analysis System, Behpajooh, Iran) coupled with a Pentium II personal computer. All studies were carried out at 298± 2 K.

3. Results and discussion

Typical cyclic voltammogram of copper in 0.5 M NaOH solution and in the potential range of -250 to 1000 mV after five cycles is shown as curve a in Fig. 1 where potential sweep rate of 10 mV s–1 has been employed. This measurement after five cycles was employed for the sake of obtaining maximum anodic current in this state. The electro-oxidation of saccharose occurs not only in the anodic but also continues in the initial stages of the cathodic half cycle, Fig. 1.

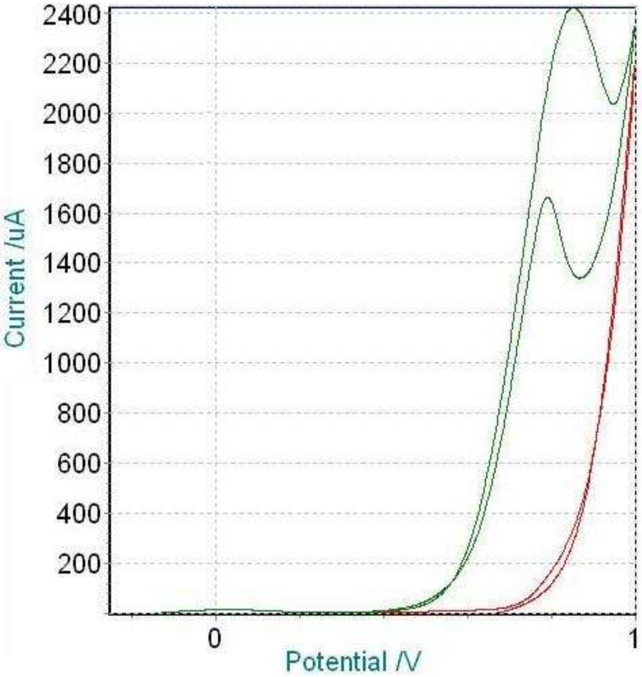

Fig. 1. Typical cyclic voltammograms of copper electrode in the potential range of -250,1000 mV in 0.5m NaOH in the absence (a) and presence (b) of 0.04 M saccharose. Potential sweep rate is 10 mV/s.

Saccharose molecules adsorbed on Cu(II) sites are oxidized at higher potentials parallel to the electrooxidation of Cu(II) to Cu(III) sites. In the reverse half cycle, the electrooxidation of saccharose continues and its corresponding current goes through a maximum due to the regeneration of Cu(II) surface species that are active sites for the adsorption of saccharose.

A mechanism for the oxidation of saccharose at copper electrode is studied:

(1) $Cu^{2+} \xleftrightarrow{k,k_{-11}} Cu^{3+}$

(2) $Cu^{3+} + saccharose \xrightarrow{k_2} \text{int}\,ermediate + Cu^{+2}$

(3) $Cu^{3+} + \text{int}\,ermediate \xrightarrow{k_3} product + Cu^{2+}$

It has been found that in the course of an anodic potential sweep the electro-oxidation of saccharose follows the formation of Cu(III) and is catalysed by this species through a mediated electron transfer mechanism [10].

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Studying of synergism effect between Multi-wall carbon nanotube and Vulcan at gas diffusion layer of gas diffusion electrode for oxygen reduction reaction

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Introduction

As a potential candidate for an environmentally benign and a highly efficient electric power generation technology, proton exchange membrane fuel cells (PEMFC) are now attracting enormous interest for various applications [1-4]. Gas-diffusion electrode (GDE) structures in polymer electrolyte fuel cell have evolved from two layers to three layer structure. Three layer electrodes are made by a porous support layer (carbon paper), a diffusion layer consisting of carbon particles and polytetrafluoroethylene (PTFE) and a catalyst layer formed by Pt/C and Nafion. The performances of the electrodes depend on many parameters one of them is related to the thickness and morphology of diffusion layer. Diffusion layer have the role of reactant permeation from flow fields to catalytic sites. Altering the composition of the diffusion layer can lead to substantial improvements in the performance of the cell.

2. Experimental

In this work, we prepared 6 electrodes, that the percentage of MWCNT (Aldrich) in diffusion layer was varied between 0 and 100 with 20 intervals and same catalyst loading. A mixed of 30 wt. % PTFE and 70 wt. % carbon particles (contain Vulcan and MWCNT) in 2- propanol (Merck), water and glycerol (Merck) was sonicated for 20 minutes by using a sonicator (Misonix model S-3000) to make the homogeneous suspension. The loading of diffusion layer was fixed 1 mg cm^{-2}. The Pt loading in catalyst layer is 0.5 mg cm^{-2}.

3. Results and discussion

Results of electrochemical experiments were show in Fig 1. By comparison the results of (with out MWCNT at GDL) with GDE 62 (100 wt% MWCNT), can observe remarkable difference in maximum current density at low potential region, (about 110 mA.cm^{-2}) and exchange current density (Fig.1 and Table1). Such as these results, the polarization and ionic resistance of GDE 62 are lower than the GDE 1 and permeability of GDE 6 is higher than GDE 62. As mentioned in previous section, these good results indicate that presence of MWCNT improved the performance of electrode. Therefore, GDE from 3 to 5 were fabricated in order to studying the synergism effect due to MWCNT and Vulcan at GDL.

Experimental results confirm presence the synergism effect, such as GDE 5 (80 wt% MWCNT at GDL) has the maximum current at low potential region (420 mA.cm^{-2}) in compared with pure states (about 55 % improvement rather than GDE 1); also the results of exchange current density, polarization and ionic resistance and permeability is the best results respect to the other GDEs (Table 1).

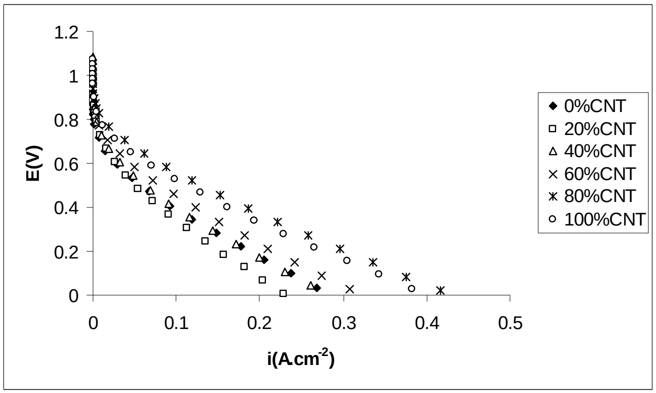

Fig 1. I-V curves for electrodes containing different MWCNT and Pt loading 0.5 mg.cm^{-2} for ORR in 2 M H_2SO_4 at 25 ^{0}C.

Table1. Exchange current dencity, permeability, charge transfer and ionic resistance of electrodes with different percentage of MWCNT and Pt loading 0.5 mg.cm^{-2}

electrode	LCD	H.C.D			
	i_0 *10^{-5} (A.cm^{-2})	i_0 (A.cm^{-2})	$D^{1/2}$*C*10^{-9} (mol.cm^{-2}.s$^{-1/2}$)	R_p(ohm)	$R_{ion}/3$ (ohm)
12	47.9	0.0258	21.5	1.8	4.464
22	46.6	0.0163	10.56	1.4	4.828
32	3.41	0.00842	22.3	1.6	3.420
42	12.7	0.0224	23.9	1.26	3.190
52	186.7	0.0501	39.9	0.71	2.97
62	83.4	0.0337	36.3	0.79	3.140

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Preparation of New GDE based on polyaniline in oxygen reduction reaction for proton exchange membrane fuel cell

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1. Introduction

Considering the high cost of polymer electrolyte fuel cell catalysts, the concept of lowering the platinium loading required to provide acceptable performance has been of paramount intrest to reasercheres in this field [1]. Therefore it is essential to enlarge the effective surface area by diminishing the size of catalyst particles and to distribute the catalyst only on the surface of the electrode for a low platinum loading and use of the whole surface of catalyst [2]. Electron conductive polymers, such as polyaniline , polypyrrole, polythiophene, are very convenient substrates in order to disperse, at the molecular level, electrocatalytic materials, in such a way that each catalytic center will be accessible to the reactive molecule. Platinum and platinum-based alloy catalysts have been highly dispersed in conducting polymers to activate various electrochemical reactions: reduction of protons [3], oxygen reduction [4], hydrogen oxidation [5], and finally oxidation of small organic molecules, such as methanol [6]. In most caces, the electrocatalytic activities of such modified metallic electrodes are greater than that of bulk metals and it is to greatly reduce the amount of platinum in the electrode and thereby significantly lower its cost, for example, for application in fuel cells and battry.

In this study: (1) Polyaniline (PANI) is coated on carbon paper with electropolymerization of aniline and trifluromethanesolfunic acid..(2)

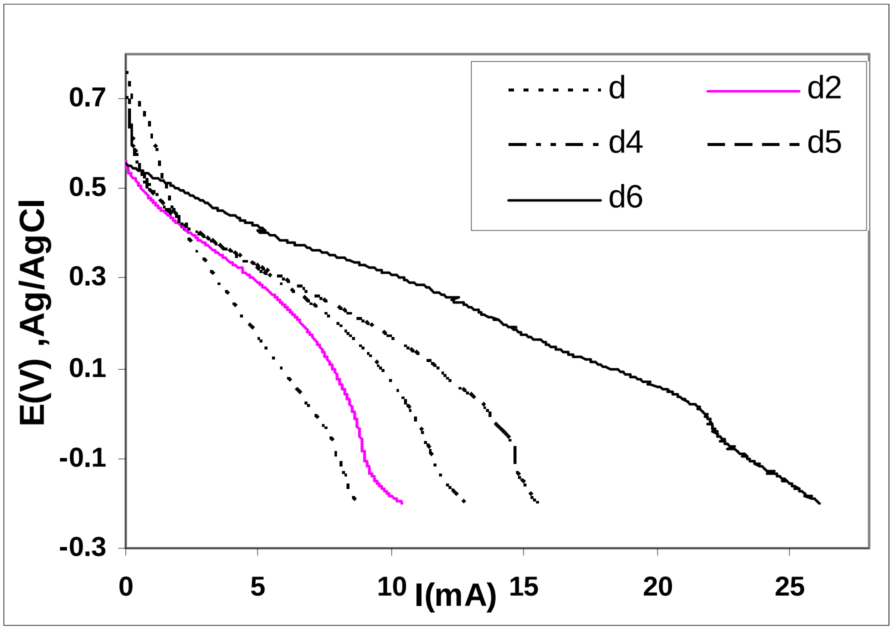
In this work PANI is pretreated at potential (0 ,0.2, 0.4 ,0.5 ,0.6 and v) for 900 S and platinum electrodeposited on the carbon-polyaniline .The effect of potential pretreatment on electrochemical behavior of GDE in ORR is investigated by I-V , EIS and SEM techniques.

2. Experimental

The polyaniline film formed on the carbon paper (TGP 060T) working electrode by the CV technique at a sweep rate of 50 mV /s between 0 and 1.1 V vs. Ag/AgCl reference electrode for 26 cycles in solutions of 0.1 M aniline + 0.5 M triflurometane solfunic acid.. After polymerization, the polyaniline film was treated in 0.5 M H2SO4 solution with constant potential (0.2,0.4 ,0.5, 0.6, 0.8 V) for 900 s. then the electrodes was soaked in the 3 mM H2PtCl6+ 0.5 M H2SO4 solution for 15 min. Finally carbon paper–polyaniline composite modified with platinum particles by CV technique (- 0.25 to 0.65 V) at 50 mV/ s for 25 cycles.

3. Result and discussion

As is well known, platinum particles can be dispersed within the conducting polymer film by cyclic potential polarization, while the structure and nature of the conducting polymer film will have a significant effect on the deposition of platinum particles [7]. Since cations and anions can be considered as aggregates consisting of the central ions and the solvated water molecules ,the movement of ions within the polymer should be impeded by solvated water , especially when the pore size of the conducting polymers is equal to or smaller than the solvated ion size. In addition, the solvated water molecules should move with the migration of ions within the polymer film. (8) By applied potential in this work the pore of polyaniline is increased so that conductivity is increased . EIS and I-V polarization curve reveal this result.



(Fig .1) polarization curve in sulfuric acid 0.5 M for d, d2 , d4, d5, d6 electrods d ,d2 ,d4 ,d5 ,d6 are the electrodes which electropolymerization by cyclic voltametry and pretreated by constant potential 0 , 0..2 ,0.4 ,0.5 , 0.6 V respectively and then electrodeposition platinum.

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Study of Dielectric Constant effects on preparation conditions of gas diffusion electrodes for Oxygen Reduction Reaction in polymer electrolyte membrane fuel cells

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Abstract

The effect of solvent dielectric constant that used for preparation of catalyst layer of gas diffusion electrode (GDE) in Proton exchange membrane fuel cell (PEMFC) cathodes for oxygen reduction was investigated. Electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV), Chronoamperometry (CA) and Cyclic Voltammetry (CV) measurements were carried out at 298K in 2.0 M H_2SO_4 on electrodes with same nafion loading and Pt loading but different solvent dielectric constant for ink preparation. In all electrodes nafion loading of 0.5 mgcm^{-2} and Pt loading of 1 mgcm^{-2} were chose. EIS supplied information on the charge transfer resistance and CV on the electrochemical active area for the oxygen reduction reaction (ORR) showed optimum results in states that dielectric constant was 4.2. The results indicate that, under optimized conditions the (solvent dielectric constant of 4.2) exchange current density and Tafel slope are 9.8×10^{-5}mA cm^{-2} and 66.0 mVdec^{-1}, respectively. Examination of morphology of the prepared electrodes using SEM confirmed that the microstructure of the catalyst layer affected with different solvent dielectric constant.

Keywords: PEMFC; Gas Diffusion Electrode; Catalyst layer; Oxygen Reduction Reaction; Dielectric Constant.

1. Introduction

Nafion ionomer is commonly used in PEMFC electrodes to enhance proton conduction from the electro catalytic metallic surface towards the polymer electrolyte. The ionomer content variation in the catalyst layer has been one of the most analyzed parameters. The nafion network structure and its interconnection throughout the electrode determine the three-dimensional zone of the catalytic layer, the triple- phase boundary and the porosity. The solvents used for inks preparation play a key role in the formation process of the proton conduction network, since the dielectric constant of solvent influence the degree of the nafion ionomers aggregation [1-2].

In the present study, we investigated the preparation condition of gas diffusion electrode with changing the solution dielectric constant that used for preparing catalyst layer in order to examination of nafion state effect on performance of GDE. For this purpose we used four electrolyte (Normal butyl acetate, Iso propyl alcohol, Isooctane, Ethyl acetate) and mixture of them for gathering desired solution dielectric constant. Catalyst inks were prepared using the selected solvents and mixture of Normal butyl acetate/Isopropyl alcohol or mixture of Normal butyl acetate/ Isooctane and then fabricated in to gas diffusion electrode using a transfer-printing technique. For studying the fabricated gas diffusion electrodes, we used cyclic voltammetery, linear sweep voltammetry, chronoamperometry, SEM and impedance techniques.

2. Experimental

Porous GDE was constructed according to a previously described procedure [3]. Catalyst inks were prepared using the selected solvents and mixture of Normal butyl acetate/Isopropyl alcohol or mixture of Normal butyl acetate/ Isooctane and then fabricated in to gas diffusion electrode using a transfer-printing technique.

The reduction of oxygen was investigated at the porous GDE (geometric exposed area 1.3 cm^2) in 2 M H_2SO_4.

3. Results and discussion

The cyclic voltammetry studies were carried out to understand the variation of electrochemical surface area (ESA) with solution dielectric constant. Table 1 summarized the charges Q_H and EAS for tested electrodes.

Table 1: The charges Q_H, roughness factor and EAS for tested electrodes

Name of Electrode	Solvent	Dielectric constant	Q_H	EAS	roughness factor
GDE1	Isopropyl alcohol(IPA)	18.3	227.516	216.6819	833.3919
GDE2	NBA: IPA(75:25)	8	149.42	142.3048	547.326
GDE3	NBA: IPA(90:10)	6.319	121.03232	115.2689	443.3418
GDE4	Ethyl acetate	6	59.9	57.04762	219.4139
GDE5	Normal butyl acetate(NBA)	5.01	206.336	196.5105	755.8095
GDE7	NBA: Isooctane(75.75:24.25)	4.3	172.357	164.1495	631.3443
GDE8	NBA: Isooctane(71.6:28.4)	4.2	196.5491	187.1896	719.9601
GDE9	NBA: Isooctane(68.06:31.9)	4.1	102.6339	97.74657	375.9484

The electrodes prepared with optimum dielectric constant solvents showed a higher performance. The main factors improving the performance were the pore electrolyte resistance in the catalyst layer and pore enlargement. The catalytic layer microstructure is closely related to the ability of the solvent for dispersing the nafion ionomer and forming fine colloidal solutions. For a given Pt and nafion loading in the catalytic layer, the electrode performance has been seen shown to be closely related to its microstructure, which is finally defined by the solvent dielectric constant. In this work electrode prepared with dielectric constant solvent of 4.2 shows the better performance.

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Analysis of the dynamic response of a tubular SOFC to the electrical load change using a 2-D transient numerical model

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Abstract

The purpose of this study is to predict the cell dynamic response in a step load current change. A 2-D transient numerical model is used to solve the transient equations of flow, energy and species conservation in a single tubular solid oxide fuel cell (SOFC). Also an electrical model is considered to compute the electrical potential and current distribution in the cell. Using this comprehensive model the dynamic behavior of TSOFC is studied. First an initial steady state operating condition is set for the SOFC model. The simulation starts when the cell is at the steady state in a specific output load. When the load step change takes place, the solution continues to a secondary steady state condition. Then the cell transient behavior is analyzed. The results show that when the load current is stepped up, the output voltage reduces to steady state in about 750s.

Introduction

Solid oxide fuel cells employ a solid-state electrolyte (usually yttria-stabilized zirconia (YSZ)) and works at high temperature, in the range of 800–1000 ◦C to reach the required high electrolyte ionic conductivity [1]. Considerable amounts of research work have been conducted to SOFC, making the SOFC close to the commercial applications. One of the problems for the application of SOFC is its relatively slow response to the input parameters time variation. Therefore, the transient analysis of the fuel cell is useful to predict the cell dynamic behavior and operation. In 1994, Achenbach [2] analyzed the dynamic operation of a planar solid oxide fuel cell. He examined the transient cell voltage performance due to temperature changes and current density with lamped assumption for the cell temperature distribution. Hall et al (1999) [3] also developed a thermodynamic model for prediction of transient operation of the Tubular SOFC. Sedghisigarchi and Feliachi [4] combined heat transfer dynamics and species dynamics to form a new dynamic model. Also Xue et al. [5], considered a one-dimensional transient model for Heat and mass transfer simulation assuming an electrical circuit include the Ohmic resistances and capacitors for the energy storage mode of operation.. Iora et al [6] considered the internal reforming/shifting reactions in fuel channel in their study. Qi et al. [7] developed a quasi 2-D model of a tubular SOFC based on the changes along the gas flow direction using the control volume (CV) approach. They obtained a non-linear set of differential equations for the heat and mass transfer as well as electrical and electrochemical variables. By solving these equations simultaneously, they calculated the cell time response to the load change. None of the developed models has considered the cell second dimension effects (r-direction) on the dynamic operation of the tubular SOFC. In this paper, we present a transient two-dimensional heat and mass transfer model to predict the cell dynamic behavior accurately.

Governing Equations and Numerical Procedure

In present work, a transient 2-D heat and mass transfer model is used for the fuel and air flow simulation, also electrolyte and electrodes. The computational domain consists of the fuel and air channels, air tube, supporting tube and electrolyte and electrode layers. The momentum, heat and mass transfer equations in polar coordinate are applied (Eqs. 1-4). Nerenst voltage and activation polarization in anode and cathode is calculated by Eqs. 5 and 6 [7].

$$\frac{\partial(\rho u)}{\partial t}+\frac{\partial(\rho uu)}{\partial x}+\frac{1}{r}\frac{\partial(r\rho vu)}{\partial r}=-\frac{\partial p}{\partial x}+\frac{\partial}{\partial x}\left(\mu\frac{\partial u}{\partial x}\right)+\frac{1}{r}\frac{\partial}{\partial r}\left(r\mu\frac{\partial u}{\partial r}\right)+\frac{\partial}{\partial x}\left(\mu\frac{\partial u}{\partial x}\right)+\frac{1}{r}\frac{\partial}{\partial r}\left(r\mu\frac{\partial v}{\partial x}\right) \tag{1}$$

$$\frac{\partial(\rho v)}{\partial t}+\frac{\partial(\rho uv)}{\partial x}+\frac{1}{r}\frac{\partial(r\rho vv)}{\partial r}=-\frac{\partial p}{\partial r}+\frac{\partial}{\partial x}\left(\mu\frac{\partial v}{\partial x}\right)+\frac{1}{r}\frac{\partial}{\partial r}\left(r\mu\frac{\partial v}{\partial r}\right)+\frac{\partial}{\partial x}\left(\mu\frac{\partial u}{\partial r}\right)+\frac{1}{r}\frac{\partial}{\partial r}\left(r\mu\frac{\partial v}{\partial r}\right)-\frac{2\mu v}{r^2} \tag{2}$$

$$\frac{\partial(\rho CpT)}{\partial t}+\frac{\partial(\rho CpuT)}{\partial x}+\frac{1}{r}\frac{\partial(r\rho CpvT)}{\partial r}=\frac{\partial}{\partial x}\left(\lambda\frac{\partial T}{\partial x}\right)+\frac{1}{r}\frac{\partial}{\partial r}\left(r\lambda\frac{\partial T}{\partial r}\right)+\dot{q} \tag{3}$$

$$\frac{\partial(\rho Yj)}{\partial t}+\frac{\partial(\rho uYj)}{\partial x}+\frac{1}{r}\frac{\partial(r\rho vYj)}{\partial r}=\frac{\partial}{\partial x}\left(\rho D_{j,m}\frac{\partial Yj}{\partial x}\right)+\frac{1}{r}\frac{\partial}{\partial r}\left(r\rho D_{j,m}\frac{\partial Yj}{\partial r}\right)+sj \tag{4}$$

$$E=\frac{-\Delta G}{n_e F}=\frac{-\Delta G^0}{2F}+\frac{RT}{2F}\ln\frac{(P_{O2}/P^0)^{0.5}(P_{H2}/P^0)}{\left(P_{H2o}/P^0\right)} \tag{5}$$

$$R_C=\frac{1}{\frac{4F}{RT}k_C(\frac{p_{O2}}{p})^{0.25}\exp(-\frac{U_C}{RT})} \quad , \quad R_A=\frac{1}{\frac{4F}{RT}k_A(\frac{p_{H2}}{p})^{0.25}\exp(-\frac{U_A}{RT})} \tag{6}$$

The conservation equations are solved numerically with control volume SIMPLE method and electrical outputs are calculated with an equivalent electrical circuit for the cell. The mesh number is 220×640 in the width and the length of the cell respectively. The solution is converged with an iterative process between electrical, electrochemical and flow solution outputs in each time step.

Results and Discussion

In order to validate our results, simulated voltage transient response to a load step is compared with the same load step, proposed by different authors, for similar parameters (Figure 1). As shown in figure the dynamic trend from present model is consistent with those from previous studies. As it is shown the simulated steady state voltage from our model is same with that calculated by Qi study [7]. However, the time that the system reaches to steady state condition is more (about 750 s) in present study. It is due to the radial gradient of the state variables (i.e. temperature and species mole fraction) and the time they need to diffuse in whole domain.

Figure 2 shows the cell temperature distribution in load current density of 3500 A/m^2 for a standard cell geometry and material [7]. The output voltage in this load current is obtained 0.7 v. The temperature distribution results show a high gradient of temperature in radial and axial direction and maximum temperature is about 1000$^{\circ}C$.

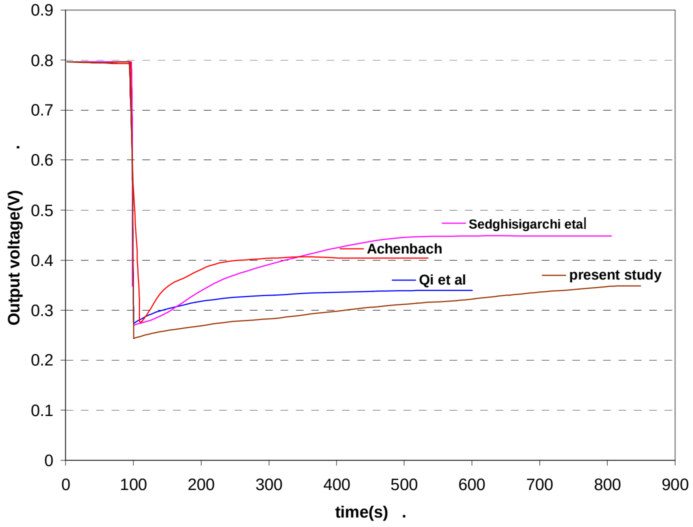

Fig. 1 the voltage responses to load step changes

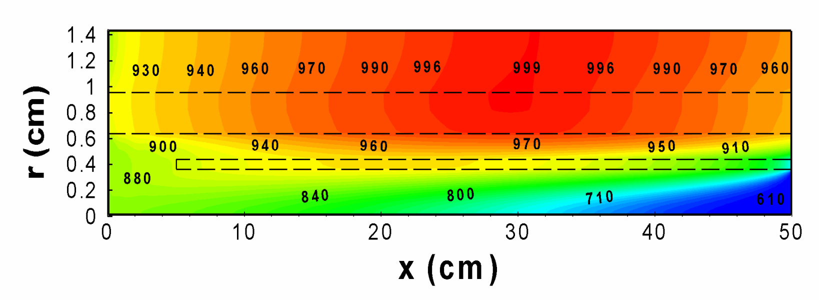

Fig. 2 the temperature distribution in Tubular SOFC

Figure 3. shows the mass fraction contours of vapor in fuel channel. In fuel channel the mass fraction of vapor increases along the fuel channel from 0.14 to

0.38 due to electrochemical reaction of hydrogen.

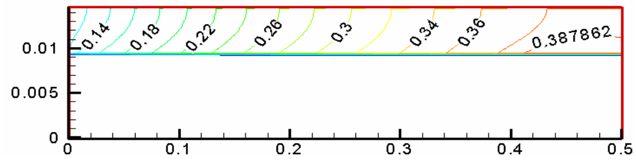

Fig. 3 vapor mass fraction contours in fuel channel

In conclusion, the presented 2-D model can predict the dynamic operation of the Tubular SOFC more accurately, due to concerning the r-direction gradients of parameters, as it is shown in results.

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Methanol electrooxidation on carbon paste electrode modified by nickel ions dispersed into poly (2,5-Dimethylaniline)

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Quantitative determination of methanol, is of great interest in food, fermentation and wine industries as well as in clinical chemistry. Methanol is one of the interesting future fuels for fuel cell application. Compared with other cells, the direct methanol fuel cell (DMFC) has several advantages such as high efficiency, very low polluting emissions, a potentially renewable fuel source and fast and convenient refueling. On the other hand, the slow kinetics of methanol is one of the unsolved problems in the development of DMFCs and represents a serious impediment in the use of electrochemical methods, based on the direct oxidation of this molecule on the electrode, with analytical purposes.

Thus, a large number of investigations have been carried out to diminish the typically large overpotentials encountered in the direct oxidation of methanol at most unmodified electrode surfaces or at chemically modified electrodes.

It is well stablished that nickel can be used as a catalyst due to its surface oxidation properties. Many electrodes involving nickel as a component in their manufacture can be used as catalyst in fuel cells. It is commonly used as an electrocatalyst for both anodic and cathodic reactions in organic synthesis and water electrolysis[1]. One of very important uses of nickel as a catalyst is for the oxidation of alcohols.

Several studies of the electrooxidation of alcohols on Ni have been reported[2]. Nickel-based electrodes obtained by chemisorption of nickel oxide/hydroxide on to glassy carbon have demonstrated long term stability in alkaline solutions and

Excellent capability to catalyze the oxidation of organic molecules. The high valence species of Ni seem to act as strong oxidizing agents for low-electroactivity organic substrates.

On the other hand, conducting polymers, a new class of electrode materials, are of considerable interest in the field of electrocatalysis. The polymers used are mainly polyaniline, polypyrrole [3,4]. These polymers offer great advantages due to their very good conducting and mechanichal properties and the good adhension to electrode substrate.

In this paper, we report the electrooxidation of methanol in alkaline medium solution using carbon paste electrode modified by a film of poly (2,5-Dimethylaniline) containing nickel. Electropolymerization at the surface of CPE using consecutive cyclic voltammetry (for 25 cycles) between 0.0 and 1.0 V at 50 mVs^{-1} was performed in sulfuric acid solution containing 20 mM 2,5-Dimethylaniline.

In order to incorporate Ni(II) ions into the P-2,5-DMA film, the freshly electropolymerized CPE was placed at open circuit in a well stirred aqueous solution of 0.2 M $NiSO_4$**.** Accumulation of nickel ions was carried out by complex formation between Ni(II) and amine sites in the polymer backbone, for a given period of time (t_a, accumulation time). Electrochemical behaviour of Ni/P-2,5-DMA/MCPE was studied by electrochemical method such as cyclic votammetry.

At last because of importance of methanol in many clinical and industrial applications، cyclic votammetric studies were carried out to investigate the electrocatalytic ability of modified electrode in alkaline solutions.

Electrochemical response of the Ni/P-2,5-DMA/MCPE in alkaline solution (i.e., 0.1 M NaOH) exhibits well defined anodic and cathodic peaks (Fig.1b) associated with the Ni(II)/Ni(III) redox couple and oxygen evolution reaction about 0.8V.

An increment in the anodic peak current for peak (P_{aI}) followed by the appearance of a new peak (P_{aII}) at more positive potential and a decrease of the cathodic peak (P_{cII}) during the reverse scan are the main effects observed upon the addition of 0.1 M of methanol to the electrolyte (Fig. 1a). We also study the effect of scan rate and methanol concentration on the catalytic current. Chronoamperometric and chronocoulometric studies as well as other electrochemical methods, was employed in this work for the invesitgation of electrode process at chemically modified electrodes.

In the alkaline medium, the [NiOOH] formed present a potent and persistent electrocatalytic activity towards methanol oxidation. According to our experimental results at low methanol concentrations the rate of the catalytic process is controlled by diffusion while at high alcohol concentrations, the reaction is governed by kinetic of the interaction between methanol and the oxidized nickel catalytic centers present in the film.

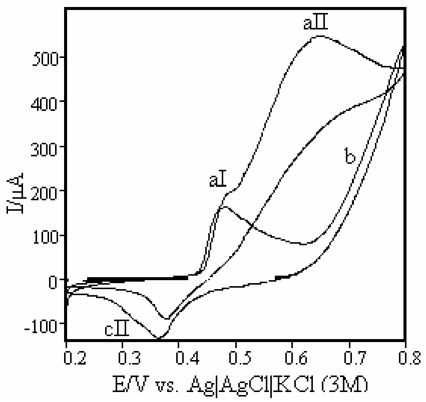

Fig. 1

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Study of electrocatalytic oxidation of ethanol in alkaline media on a nickel/polymer modified carbon paste electrode

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The electrooxidation of ethanol is considerably interest, as in terms of its importance for practical electrocatalytic application in liquid fuel cells and because of its similarity to methanol [1]. It was also found that ethanol has comparable electrochemical activity to that of methanol. Since ethanol is a product which could be obtained from renewable sources, it is of special interest for chemical industries.

The mechanism and kinetics of ethanol oxidation have been studied under a wide range of conditions and on various electrodes [2, 3]. Among them, nickel is an effective and cheap catalyst for ethanol electrooxidation [4, 5].

In this work, poly (N-methylaniline) was prepared by electropolymerization of aqueous solution of monomer at the surface of carbon paste electrode using galvanostat method. Then Ni (II) ions was incorporated into the polymeric film by immersion of the electrode in $NiSO_4$ solution.Therefore poly (N-methylaniline)-nickel modified carbon paste electrode (Ni/PNMA/MCPE) was prepared. The surface coverage ($\Gamma=1.4\times10^{-4}$mol cm^{-2}) of immobilized active substance i.e. Ni (II), in film was evaluated by cyclic voltammetry.

The effect of scan rates on electrochemical properties of Ni/PNMA/MCPE was investigated. Our results revealed that the electrochemical process is diffusion controlled. This modified electrode was used as anodic material for electrooxidation of ethanol in 0.1 M NaOH solution. The electrocatalytic activity of the electrode for oxidation of ethanol has been explained by examining of cyclic voltammetry and chronoamperometry measurements. The peak oxidation of ethanol on this modified electrode was observed in 0.48 V vs. Ag| AgCl| KCl (3 M), where the Ni $(OH)_2$/NiOOH transformation was occurred, while there is no peak for oxidation of ethanol at the bare carbon paste electrode. The rate constant for catalytic reaction of ethanol at the surface of modified electrode ($k_{s=}$24.4 $M^{-1}S^{-1}$) was evaluated using chronoamperometric study. The effect of ethanol concentration on the anodic peak was studied. It exhibited that the potential of Ni (II)/Ni (III) redox is slightly delayed with increasing ethanol concentration. This may be related to high Ni (II)/polymer electron transfer resistance, as ethanol absorption occures on the Ni (II) active sites. It showed that the peak height of ethanol increases linearly with increasing ethanol concentration up to 0.2 M. It can be assumed that the increase is due to the presence of a diffusion–controlled process, that plays an important role at low ethanol concentrations, while at higher concentrations, the catalytic process rate depends on the reaction between ethanol and Ni (III) species.

Furthermore the effect of scan rate on the anodic peak potential of ethanol was also studied.We observed the peaks potential shifted to positive potentials, suggesting a kinetic limitation in the reaction between the redox sites of Ni and ethanol.

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Laboratory Preparation of Multi-walled carbon nanotube-supported Pt-Ru anode catalyst and investigation of its performance in methanol oxidation in fuel cell

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Abstract

Fuel cells are clean, efficient, and noiseless. There is increasing interest in the development of fuel cell systems due to thir profound commercial applications. Particularly, direct methanol fuel cells (DMFC) can be used as dependable and long-lasting portable power sources to replace batteries, which suffer from low energy capacities and short runtime, in various electronic equipments. DMFCs strongly depend on the use of Pt electrocatalyst for effective oxygen reduction and Pt-Ru electrocatalyst for methanol fuel electrooxidation. The use of bi-or multi-component anode catalysts for methanol electrooxidations an effective way to solve the catalyst poisoning problems caused by CO and other reaction intermediates under low-temperature reaction conditions. Conventionally, high conductive carbon backs, such as Vulcan XC72 with high surface areas are used as supports for electrocatalysts to ensure large electro-reaction surfaces and good electronic conduction. Formation of electrocatalysts on CNT for membrane fuel cell applications is commonly conducted using reductive deposition methods.

In this work, we prepared carbon nanotube-supported Pt-Ru (Pt-Ru/CNT) with a desired electrocatalyst composition using a modified polyol method. The prepard Pt-Ru/CNT ecelctrocatalyst has a composition close to the intended 20wt.%Pt-10wt.%Ru and physical characteristics of prepared Pt-Ru/CNT ecelctrocatalyst was performed by X-ray diffraction (XRD) spectroscopy and

electrochemical investigation on the prepared Pt-u/CNT electrocatalyst with respect to methanol electrooxidation was carried out using cyclic voltametry. The results of this study clearly show that prepared electrocatalyst is about nanometric scale and have a good performance on electrooxidation of methanol. Overall, the prepared Pt-Ru/CNT s suitable for uses in DMFCs as an anod electrocatalyst due to distinguished characteristics of CNT and the excellent electrocatalyst morphology with the right composition.

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Development of Low Cost Direct alcohol Fuel Cells (DAFCs) for Portable and Automotive Applications

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Keyword; DAFC (direct alcohol fuel cell), fuel cell stack, Nanostructure, Alcohols oxidation.

The high cost of platinum has previously prevented fuel cell technology from competing with current energy technologies on a price-competitive basis. Limitations on future platinum supply will also drive negative economies of scale: more fuel cells that are produced, the more expensive the platinum component will be needed.

Another commercial barrier for fuel cells is the challenge associated with the fuels used for platinum-catalyzed fuel cells, namely methanol which has restrictions on sale and transportation as it is toxic; and hydrogen which is an inefficient fuel to transport, store and distribute due to its natural gaseous state.

New class of catalysts (HYPERMEC™) has developed by Acta Company, being made of a blend of other transition metals, including cobalt, nickel and iron. These metals are abundant and the pricing is vastly cheaper than platinum. They are not vulnerable to carbon poisoning and the manufacturing process is robust and scaleable.

They offer excellent performance. This enables the use of cheaper metals and less material at lower temperature and allows the use of ethanol and other fuels: Ethylene Glycol, Glycerol, n- Butanol, Isopropyl alcohol and Methanol.

The aim of this work is to evaluate low cost catalysts (HYPERMEC™) in direct alcohol fuel cells for portable and automotive applications. OH form anion-exchange membrane was used as membrane.

The test results under steady state conditions indicate DAFCs exhibit excellent performance with different types of fuels (figure 1) and also good stability in different operational conditions. Figure 2 indicates direct ethanol fuel cell stack which is applied in the small car for Shell Eco-Marathon (May 2007) as first test drive of direct ethanol fuel cell vehicle. All MEAs made by low cost catalysts (HYPERMEC™) in anode and cathode sides.

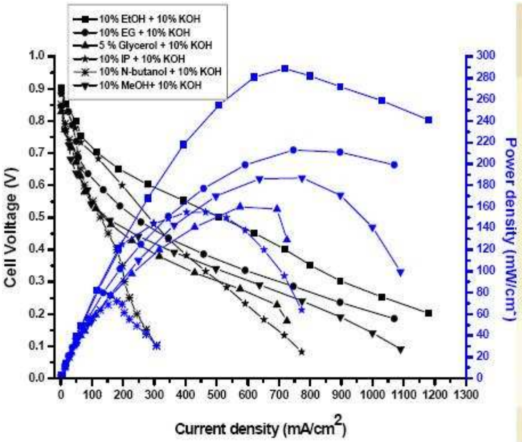

Fig 1. The performance of the DAFCs with different fuels at 80 oC

Fig 2. Direct ethanol fuel cell stack of

Experimental data, single and stack, in different conditions conclude direct alcohol fuel cells using low cost catalysts are expected to give superior potential for in portable and automotive applications.

study of gas diffusion electrode by using platinum nano particle and nafion/ polyaniline as a catalyst layer

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Introduction

There has been considerable speculation that conducting polymers would be useful catalyst support for fuel cells in few recent years. [1]. The interesting chemical behavior of the conducting polymers is due to their intrinsic redox properties, high electronic conductivity, and permeability to electroactive species [2].

Our group has done the pioneering studies that are introduction of polyaniline in gas diffusion electrodes [3].The presence of PANI instead of Nafion increases current density, catalyst utilization and reduces the polarization resistance of the GDE due to the electronic conductivity of PANI and proton conductivity [4]. In another study a gas diffusion electrode with a catalyst layer containing a mixture of Nafion and PANI nanofiber was prepared. The resulting GDE had good mechanical properties and acceptable electrochemical activity [5].

In this work we investigated GDEs which have different mole ratios of Nafion and PANI in their structure to find an optimal point for PANI–Nafion combination for oxygen reduction reaction.

Experimental

polyaniline was prepared and “doped” according to literature procedures [7] Electrodes were prepared by brushing procedure [8].

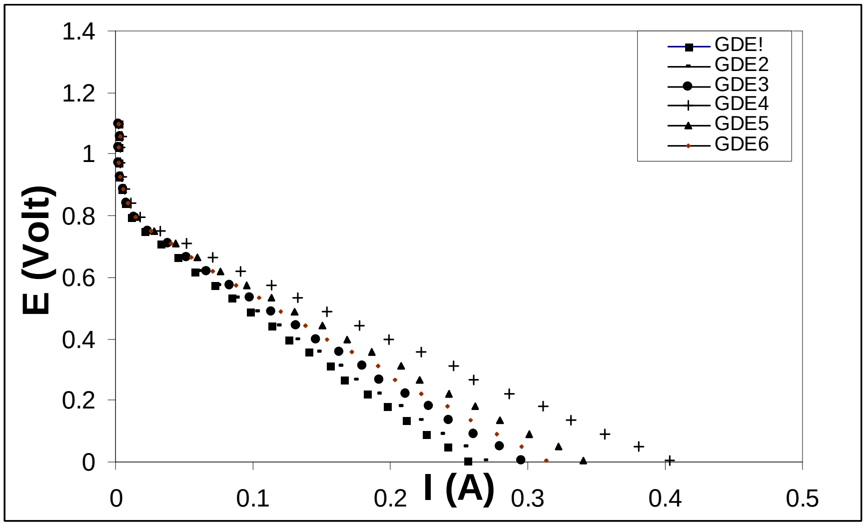
Using platinum on carbon (Vulcan) (%10 Pt/C) catalyst (carbon powder (Vulcan XC-72, Cabot) carbon paper substrate, glycerol, poly-tetrafluoroethylene(PTFE) solution, Nafion solution and PANI. Six electrodes with the same loading of diffusion layer and catalyst ,but different content of Nafion/PANI, whereas sum of Nafion / PANI loading is 1mg/cm^2 were prepared. The properties of gas diffusio electrodes are citedTable 1.

GDE	Diffusion layer mg/cm^2	Catalyst layer mg/cm^2	PANI mg/cm^2	Nafion mg/cm^2
۱	۱	0.5	۰	۱
۲	۱	۰,۵	۰,۲	۰,۸
۳	۱	۰,۵	۰,۴	۰,۶
٤	۱	۰,۵	۰,۶	۰,۴
٥	۱	۰,۵	۰,۸	۰,۲
٦	۱	۰,۵	۱	۰

Table1.Gas Diffusion Electrodes properties

Result and Discussion

The polarization curve for oxygen reduction obtained at 25 ^{o}C, potential range -0.3–1 volt . Fig 1 shows polarization curves for electrodes.



Analysis of experimental polarization data was made using Tafel equation [1]. Table2 is observed the electrochemical parameters derived Tafel equation

GDE	OCV mV	b mVdec^{-1}	$I_{0.}10^{-5}$ Acm^{-2}
١	٧٠٨	١٢٢	٢,٣
٢	٧٢٠	105	٣,٠٢
٣	٧٤٥	٩٦	٣,٨
٤	٨٠٥	٦١	۴,٣
٥	٧٨٠	٨٥	٣,۵
٦	٧٦٢	١٠٠	٣,٣

Incorporation of PANI to gas diffusion electrode and reduction of Nafion content increase current density of GDE_1-GDE_4 This means, GDE_4 is optimum point for combination of Nafion/PANI in gas diffusion electrode. In this point electrochemical behavior of GDE is better than electrodes containing PANI or Nafion slightly. Existence of PANI in electrode improves electron transfer, in as much as PANI is an inherently conducting polymer, it can improve electron carrier in catalyst layer, thus the more electron needs the more proton to react, therefore Nafion is forced to conduct more proton, and its saturation state decreases. This interaction between Nafion and PANI affected mass transport, gas permeability, and activity of catalyst, consequently enhanced the three dimensional reaction Zone. However further decreasing of Nafion and excess increasing of PANI makes electrode performance poorer. This is may be due to blocking of the catalyst by the high thickness of PANI, reducing gas permeability, and poor contact of the electrolyte with catalyst.

Conclusion

The target of this work was to find optimum point of mixture of PANI and Nafion in the structure of gas diffusion electrode fabricated in the previous work

1-Performance of the gas diffusion electrode including PANI is better than the one including the Nafion slightly.

2-The electrochemical activity of electrodes containing both Nafion and PANI was more than the electrode including PANI alone.

3- The point, in which the mole ratio of PANI was %60 and Nafion was %40 was the optimum for the mixture.

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A study of the electro-catalytic oxidation of methanol on a manganese dioxide modified glassy carbon electrode

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Abstract

Manganese dioxide modified glassy carbon electrodes prepared by cycling the potential of a glassy carbon electrode in acidic solution exhibited electrocatalytic activity for the oxidation of methanol in acidic media. The methods of cyclic voltammetry (CV) have been employed. The mechanism of methanol oxidation has also been discussed in terms of the formations of intermediates normally encountered in small organics electro- oxidation.

1. Introduction

It has been proposed that the direct methanol fuel cell (DMFC) is a promising power source in electric vehicles [1]. Methanol is the one being most intensively investigated at present, from the different small organic molecules. Methanol oxidation reaction has been the subject of a large number of studies in the past, for the facts that it is a relatively high energy density fuel, it is liquid at ambient temperature, is of low cost and available at industrial scale and the infrastructures for production and distribution are already available [2]. Different catalysts for DMFC have been studied, but Pt and Pt group metals are found to be most successful [3] high costs of these materials are often very prohibitive. In the present investigation, modified manganese dioxide is used as potential materials for the electro catalytic oxidation of methanol.

2. Experimental

2.1. The chemicals all chemicals used in this work were Merck products of analytical grade and were used without further purifications. Doubly distilled water was used throughout.

2.2. The cell and instrumentations electrochemical studies were carried out in a conventional three-electrode cell powered by an electrochemical system comprising of EG & G model 1278 Potentiostat/ Galvanostat and Solartron model 1255 frequency response analyzer. It was run by a PC through ZPLOT/ZVIEW commercial software via a GPIB interface. The potentials were measured against an Ag/AgCl saturated reference electrode with a Pt wire forming the counter electrode and a glassy carbon disk electrode of 2 mm diameter (modified) used as a working electrode. All studies were carried out at 308 ± 2 K. For preparing the modified electrodes, first, the GC disk electrode was further polished with 0.05 μm à-alumina powder on a polishing micro-cloth and rinsed thoroughly with doubly distilled water prior to modification. Then, it was placed in a solution containing 0.1M $MnSO_4$ + 0.5 M H_2SO_4 under the regime of cyclic voltammetery where 50 consecutive cycle in the range of -100 to 150 mV/ Ag,AgCl and a potential sweep rate of 100 mV/s were applied to preparing the modified electrodes.

3. Results and Discussion

A cyclic voltammogram on a modified GC working electrode in 2M H3PO4 is present in Fig. 1. Two anodic peaks were observed at -0.6 V/Ag, AgCl, is probably due to the adsorbtion of oxygen related to the oxidation of Mn2+ to MnO2 [5]. The cathodic peak of 0.9 V/Ag, AgCl is related to the regeneration of Mn2+ species.

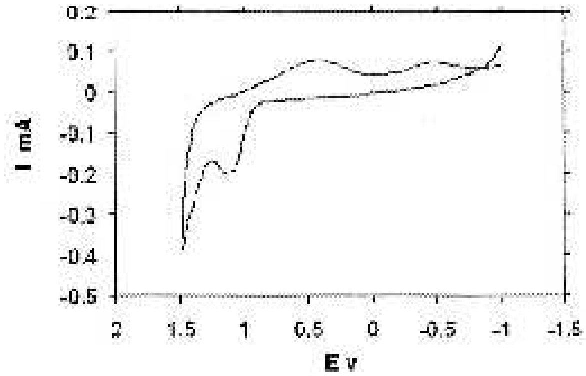

Fig.1. Cyclic voltammogram of the modified GCelectrode in 2M H3PO4 solution with a potential sweep rate of 100 mVs-1.Modification of the GC surface is carried out by 50 cycles in the synthesis solution: 0.1 M MnSO4 + 0.5 M H2SO4. 100 mVs-1.

Fig.2. presents the CVs of modified electrode both in the absence (a) and in the presence of 0.5M methanol and Fig.3 presents the CVs of modified electrode both in the absence (a) and in the presence of excessive concentrations of methanol in 2M H3PO4 solutions. In the presence of methanol, both anodic and cathodic peaks enlarge. These indicate that methanol is oxidized in the anodic sweep and as methanol is not electroactive in the potential window, it seems that its oxidation is mediated by the surface high valence manganese species. The significant current in the reverse sweep indicates that the electro-oxidation of Mn species to higher valence state is much faster than the catalytic oxidation of methanol.

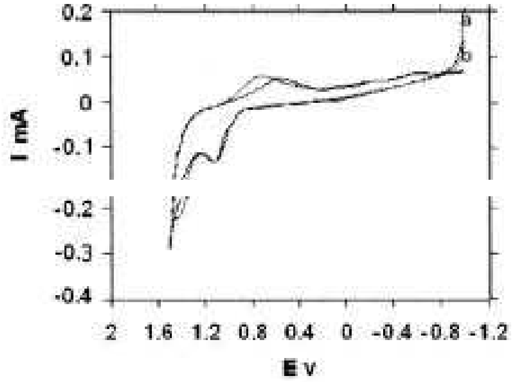

Fig.2. Cyclic voltammogram of the modified GCelectrode in 2M H3PO4 in the absence (a) and in the presence of 0.5M methanol. Potential sweeprate is 100 mVs^{-1}.

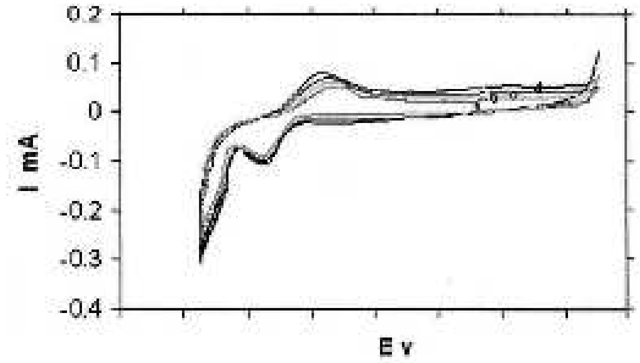

Fig.3. Cyclic voltammogram of the modified GC electrode in 2M H3PO4 at different methanol concentrations: 0.1 M (a); 0.25 M (b); 0.3 M (c); 1M (d), respectively. Potential sweep rate is 100 mVs^{-1}.

Fig.4 presents the CVs in the presence of 0.5M methanol recorded at various potential sweep rates. As the sweep rate increases, the anodic and cathodic peaks enlarge which indicate that the rate of the electro-oxidation of Mn species to higher valence state and the rate of catalytic oxidation of methanol both rise as a result.

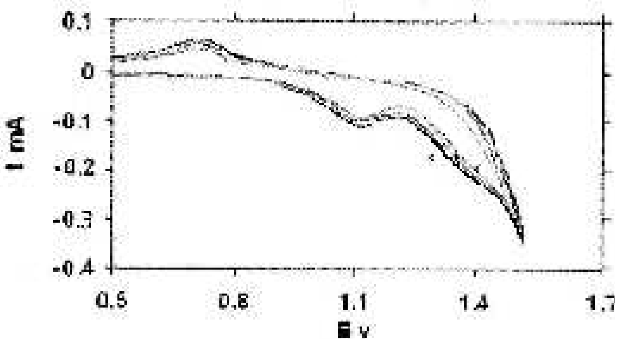

Fig.4. Typical cyclic voltammogram of themodified GC electrode in 0.5 M methanol+2M H3PO4 at different potential sweep rates: 50(a); 100(b); 150(c); 200(d) mVs-1.

On the basis of our study and consistent with the literature [5-6] the following mechanism is proposed for the mediated electro-oxidation of methanol on the modified electrode. The electro-oxidation of Mn2+ in the potential window:

$Mn^{2+} \rightarrow Mn^{4+} + 2e^{-}$

is followed by the oxidation of methanol:

$Mn^{4+} + CH_3OH \rightarrow \text{intermediates} + Mn^{2+}$

$Mn^{4+} + \text{intermediates} \rightarrow \text{products} + Mn^{2+}$

4. Conclusion

This work presents the preparation and usefulness of Manganese dioxide modified glassy carbon electrode for methanol electro-oxidation in acidic media. The electrode was electrocatalytically active around 700mV/Ag, AgCl where the GC electrode possessed no activity.

Acknowledgements

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Novel Sulfonated Copolyimides as a Candidate for Proton Exchange Membrane Fuel Cell

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Introduction

Proton exchange membrane (PEM) fuel cells (polymer electrolyte membrane) are one of the most important types of fuel cells that employ a solid polymer electrolyte to separate the fuel from the oxidant. During last decades different polymers with various structures have been reported for application as membrane in stationary or mobile fuel cell systems. Sulfonated polyimides, polysulfones, polystyrenes, polybenzimidazoles, poly(ether ether ketone)s are some of the main types of membranes have been used recently [1,2]. Polyimides with appropriate ion-conducting sites are one of the best candidates for fuel cell membrane [3,4]. Here we intend to describe the preparation of some new sulfonated copolyimides as fuel cell membranes. Polyimide membranes with various degrees of sulfonation were prepared from a new sulfonated diamine (*3,3'-Disulfonic acid-bis[4-(5-amino-1-naphthoxy)phenyl]sulfone* or DANPS), two new unsulfonated diamines (*4,4'-(5-amino-1-naphthoxy) diphenylsulfone* or ANDS, and *4,4'-(4-Aminophenoxy) diphenylsulfone* or APDS), and a six-membered ring dianhydride (NDA).

Experimental

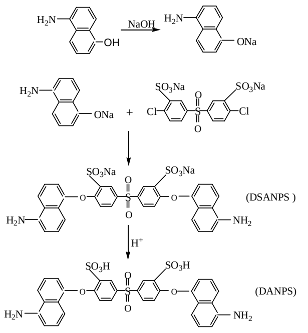
Preparation of monomers was carried out according to our published report [5].

Synthesis of sulfonated copolyimides: A typical procedure for the preparation of sulfonated copolyimide with 50 mol % degree of sulfonation based on DANPS and APDS as sulfonated and unsulfonated diamines was as follows: DANPS (2.076 g, 3.000 mmol), 30.00 mL of m-cresol, and 1.000 mL (7.200 mmol) of triethylamine were charged into a flask equipped with a Dean-Stark trap and a nitrogen inlet tube.

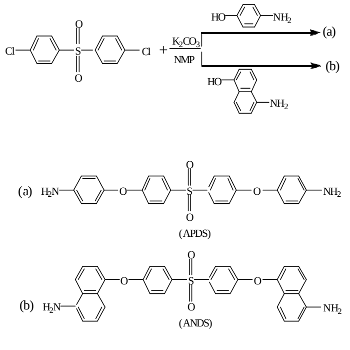
The solution was stirred for about 6 h until complete dissolution of diamine. After that, 1.609 g (6.000 mmol) of NDA, 1.296 g (3.000 mmol) of APDS, 1.464 g (12.00 mmol) of benzoic acid, and 10.00 mL of m-cresol were added to the reaction mixture and it was heated to 80 ˚C for 4 h. The temperature was increased to 180 ˚C and maintained for 10 h. Isoquinoline (1.548 g, 12.00 mmol) was added to the mixture and heated for additional 10 h. After cooling, the mixture was precipitated in 250.0 mL of isopropyl alcohol and stirred for several hours. Then it was filtered and dried. The yield of reaction was about 98 %. The same procedure was repeated for synthesis of other copolymers based on APDS and ANDS as unsulfonated diamines and with different degrees of sulfonation (40-80 mol %).

Results and discussion

We designed and prepared three diamines, a sulfonated (DANPS) and two unsulfonated diamines (APDS and ANDS), and polycondensed these monomers with a six-membered ring dianhydride (NDA) to produce related sulfonated copolyimides. The monomers were prepared according to the schemes 1 and 2:

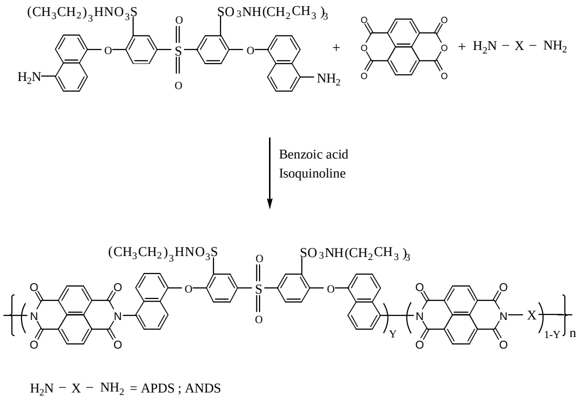


Scheme 1. Preparation of DANPS



Scheme 2. Preparation of APDS and ANDS diamines

Two series of sulfonated copolyimides with 40-80 % sulfonation content were prepared via one step polycondensation reactions of DANPS, APDS and ANDS with NDA as six-membered ring dianhydride (Scheme 3). Sulfonic acid units situated in the backbone of these copolyimides are responsible for conducting of protons and therefore ion exchange capacity of fuel cells.



Scheme 3. Preparation of sulfonated Copolyimides

The molecular weights of the copolymers were determined using GPC method in DMF and copolymers showed reasonable molecular weights (Mn = 26100 -35600). The ion exchange capacity (IEC) of the copolyimides was measured via titration method. It was in the range of 1.51-2.15 equiv./g which was increased by increasing the percentage of sulfonated units of the copolymers. Polymers showed high thermal stability based on Thermal gravimetric analysis (TGA). The initial decomposition temperature (T_0) of them was in the range of 258-310 ˚C and temperatures for 10% weight loss (T_{10}) which is an important criterion for the evaluation of the thermal stability were about 396-448 ˚C. Based on mechanical tests polymers firstly showed elastic behavior with high strength and modulus, and then tough thermoplastic behavior with low elongation.

The water uptake of polymers was measured at 30 ˚C and it was about 15-70 % based on sulfonation content of copolymers.

Presence of ether, sulfone, and bulky naphthyl groups in addition to aromatic character of the diamines made it possible to prepare copolyimides with improved solubility and processability while maintaining thermal stability and ion-exchange capacity.

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Micro fuel cells, fundamentals, recent developments, Potential Operational and Performance Issues

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1. Abstract

Micro fuel cell (MFC) refers to small fuel cells that are designed to power portable electronics equipment, and in many cases can be integrated into the electronic device itself. A micro fuel cell is a portable source of energy that converts chemical energy of a fuel into useable electrical energy under ambient conditions. In general it generates power through the electrochemical oxidation of a fuel on a catalytic surface. The oxidant is generally air or oxygen. The fuel in a micro fuel cell generally refers to methanol, a form of alcohol, a safe, non-combustible, inexpensive, renewable, plant based energy source. Micro fuel cells offer cheap and easy means to power electronic devices by simple refuelling, enabling continuous use when travelling with no access to the power grid. In this review we investigate fundamentals, recent developments of micro fuel cells.

2. Introduction

The advent of microelectromechanical systems (MEMS), micromachines, microsystems, integrated passive components and low power electronics for various types of functionalities has resulted in a surge of research in the development of power sources of matching configuration to meet the device requirements. The increasing demand for a wide variety of commercial, portable, electronic appliances such as cellular phones, laptop computers, personal organizers, digital cameras, portable radios, notebook computers, personal digital assistants, embedded monitors, military devices and specialized devices such as autonomous sensors, clinical and diagnostic test devices, micro-analytical systems, global positioning systems etc., has spurred the development of micro power sources. Since energy is stored in a fuel cell as a reservoir of fuel rather than as an integral part of the power source, fuel cells are expected to provide higher total energy for a given size or weight than batteries, calculated as Watt-hours per liter (Wh/1) or Watt-hours per kilogram (Wh/kg) due to the high amount of energy that can be stored in fuels such as hydrogen, sodium borohydride, methanol, ethanol, hydrocarbon. A second advantage of fuel cells is that once the fuel is consumed, it can be replenished instantly and the system continues to provide power. In fact, a fuel cell will continue to supply power indefinitely as long as fuel and air (02) are supplied. As a result along with the evolution of various electronic devices, the miniature fuel cells have emerged as a possible power source through the endless pursuit of ever-higher levels of performance, density and functionality. The fuel cell industry is experiencing a very dynamic development especially in the area of micro fuel Cells Micro fuel cell (MFC) refers to small fuel cells that are designed to power portable electronics equipment, and in many cases can be integrated into the electronic device itself. A micro fuel cell is a portable source of energy that converts chemical energy of a fuel into useable electrical energy under ambient conditions. In general it generates power through the electrochemical oxidation of a fuel on a catalytic surface. The oxidant is generally air or oxygen. The fuel in a microfuel cell generally refers to methanol, a form of alcohol, a safe, non-combustible, inexpensive, renewable, plant based energy source. Micro fuel cells offer cheap and easy means to power electronic devices by simple refuelling, enabling continuous use when travelling with no access to the power grid. Traditionally, fuel cells have been too big and expensive for smaller devices. Micro fuel cell faces lot of challenges, which researchers are trying to overcome. The performance of micro fuel cells should approach or exceed that of its macro counterpart for it to be attractive. Micro fuel cell technologies should preferably be self sustaining in its operation and shall be self regulating without the need for complex plumbing for fluid circulation for thermal and water management for it to be compact and autonomous.

3. Recent Developments in Micro Fuel Cell

For the realization of micro fuel cell, a combination of one or more of the following solutions have been tried by commercial industries and academic institutions involved in the active research and development activity.

1. Substrate material compatible with microelectronic fabrication: Silicon wafer, Glass, ceramic, glass epoxy laminates (PCB), organic polymers as substrate materials instead of traditional high density non-porous graphite material
2. New electrolyte formulation: Non-fluorinated ionomer membranes such as phosphazene, arylene, poly(benzimidazole) or PBI, hydrocarbon polymers, nanoporous silicon membranes to serve as proton conductors
3. Microfluidic fuel cell: liquid-liquid interface-elimination of polymer electrolyte membrane
4. Micro-scale fabrication technologies
5. Elimination of plumbing
6. Enhanced catalytic activity for the desired electrode reactions—use of carbon nanohorn
7. Ceramic based fuel reformer, micro reactors
8. Selection of fuel Typical V/I characteristics of a micro fuel cell is shown in Fig.1:

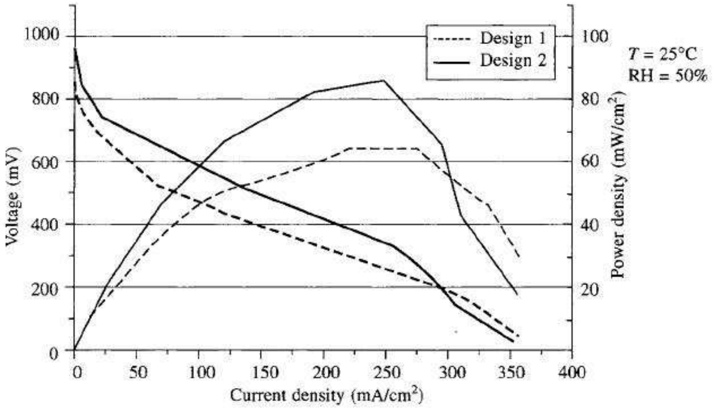

Fig. 1 *V/I* characteristics of a typical micro fuel cell.

The exploded view of the micro fuel cell assembly is shown in Fig. 2 :

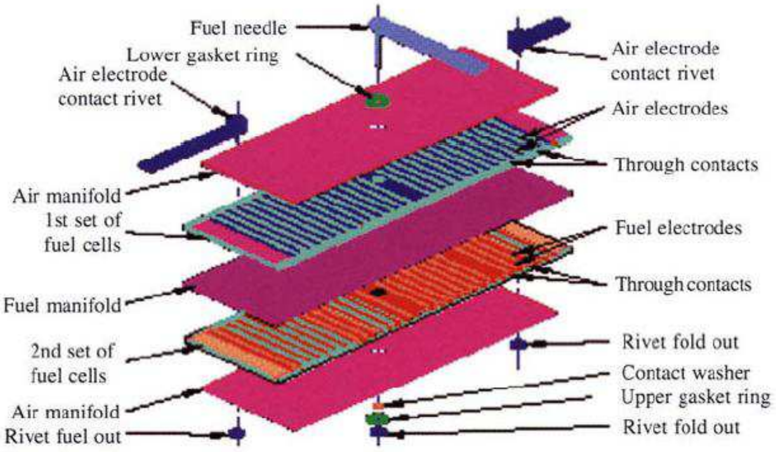

Fig. 2 Exploded view of the micro fuel cell assembly.

4. Conclusions

Micro fuel cell system faces numerous challenges for its widespread application in mobile devices. The electrical interfaces and the size of the fuel cell system should be maintained same as that of batteries. Fuel cells lack size-related standards similar to the one available for batteries. There is no standard fuel cell product that can be used as a power pack for all brands of the same electronic device. Currently micro fuel cells are quite expensive due to the use of noble metal catalyst and tiny pumps, fans, valves etc. for the reactant supply, recirculation, thermal, water management and product handling. Air traffic regulation could prohibit use and transportation devices fitted with micro fuel cells due to the flammable nature of most of the fuels used in these devices. The peak power rating of many of the micro fuel cells are inferior to that of batteries resulting in their inability to meet some of the functional requirement of microelectronic devices. Micro fuel cell system faces numerous challenges for its widespread application in mobile devices. The electrical interfaces and the size of the fuel cell system should be maintained same as that of batteries. Fuel cells lack size-related standards similar to the one available for batteries. There is no standard fuel cell product that can be used as a power pack for all brands of the same electronic device. Currently micro fuel cells are quite expensive due to the use of noble metal catalyst and tiny pumps, fans, valves etc. for the reactant supply, recirculation, thermal, water management and product handling. Air traffic regulation could prohibit use and transportation devices fitted with micro fuel cells due to the flammable nature of most of the fuels used in these devices. The peak power rating of many of the micro fuel cells are inferior to that of batteries resulting in their inability to meet some of the functional requirement of microelectronic devices.

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The Sources of Fuel Cells

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A fuel cell is a compatible technology with environment, for production of energy with high yield efficiency and the least amount of environment pollution. A fuel cell is an electrochemical conversion device, as a result of fuel cell function, chemical energy of fuel changes into electrical energy. One of the most important elements of fuel cells is source of materials used to produce electricity. The main employed sources in fuel cells are hydrogen and oxygen. Hydrogen is such as available from different sources, methanol, ethanol, natural gas, propane, petroleum, coal, gazoline, petrol and microbial and biological sources. Oxidants for fuel cell are air and oxygen with platinum catalyst. In microbial fuel cells, motor power is an oxidation reactions and reduction of a primary substance from kind of carbohydrate such as glucose. In This paper we discuss about several sources used in fuel cells as well as their advantages and disadvantages.

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Comparative study of oxidation of methanol, ethanol, 1-propanol, 2-propanol on Ni electrode

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Introduction

The electro-oxidation of alcohols is a wide research area for the development of fuel cell in this respect, a great interest exist in the studying different alcohols[1,2]. in this context , the mechanism of electrooxidation of Four alcohols (methanol, ethanol, 1propanol, 2propanol)on Ni electrode are studied .The importance of alcohols oxidation and the application of them in the fuel cell is very extreme [3,4]. According to these proposes; we compared alcohol oxidation on Ni electrode, by using cyclic Voltammetry and impedance spectroscopy techniques.

Experimental

Sodium hydroxide and all alcohols used in this work were Merck products of analytical grade and were used without further purifications. Doubly distilled water was used throughout.

Electrochemical studies were carried out in a conventional three electrode cell powered by an electrochemical system comprising of EG&G model 273 potentiostat/galvanostat. The system is run by a PC through M270 commercial softwares via a GPIB interface. A dual Sat’d Ag/AgCl, a Pt wire and a nickel disk electrode were used as the reference, counter and working electrodes, respectively. All studies were carried out at 298± 2 K.

The nickel disk electrode (2 mm diameter) was polished with 0.05 μm alumina powder on a polishing micro-cloth and rinsed thoroughly with doubly distilled water prior to modification.

Results and discussion

Ni modified NiOOH electrode prepared after repetitive cyclic Voltammetry. The fifty cycles is best qualification and optimum NaOH concentration is 0.1 M. In the presents of four alcohols a new anodic peaks with a large current is observed.

Fig. 1. Shows the cyclic voltammograms of Ni electrode in the absent and the present of .1 M methanol, ethanol, 1propanol, 2propanol.

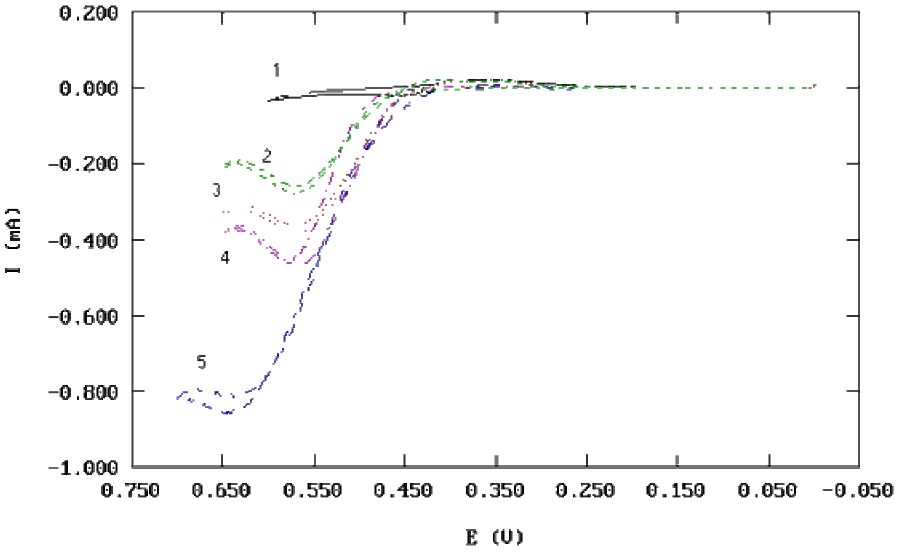

Fig. 1. Cyclic voltamogram of Ni electrode in absence (1) and presence of 1 M (2) 2– propanel, (3) ethanol, (4) 1-propanol, (5) methanol.the scan rate is 10mV $s^{-1.}$

It is observed clearly that the anodic peak currents of four alcohol is different. According to these four graphs we understand that the efficiency of methanol in low concentration is lower than the others .but by increasing the concentration the peak current of methanol was raised.

In the low concentration the peak current of methanol, 1-propanol, 2-propanol is approximately equal, but by raising the concentration of alcohol the peak currents of methanol and 1propanol were raised quickly but the current increase for ethanol and 2-propanol in that are oxidized by Ni(III) was slower than the others.

It is observes that the methanol peak is higher than the other alcohol after that the peak currents of 1-propanol, ethanol and 2-propanol were obtained respectively.

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Effect of precursor’s proportion on the properties of 8YSZ nanoparticles as an electrolyte for SOFCs

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Introduction

Current developments in SOFCs concentrate mainly on increase the durability and lowering the cost of the system and materials therein. A way to reach this goal is to decrease the operating temperature without incurring performance losses rather than further increasing the performance of the cell [1].

SOFCs are composed of three parts: cathode (air electrode), electrolyte, and anode (fuel electrode). The solid oxide electrolyte must isolate the two gas phases (fuel and air) from each other and transport oxygen ions, reduced in cathode, without significant losses from the cathode to anode. Therefore, electrolytes need to be a sufficiently fast oxygen ion conductor [1-2].

The transport of oxygen ions in the electrolyte occurs via oxygen vacancies in the oxygen sublattice. The concentration of vacancies and their mobility determines the electrolyte ion conductivities. Among number of metal oxides ion conductors may refer to zirconia stabilized with yittria in the conductive cubic phase (YSZ) [1].

Several chemical and physical methods have been devised to synthesize cubic ZrO_2, such as thermal decomposition, chemical evaporation, sol-gel methods, precipitation and co-precipitation from a solution and hydrothermal techniques [3].

Chemical methods have an important place among the experimental methods because of using relatively nonaggressive diluted solutions at moderate temperatures and no need to expensive equipment [4].

In this project, attempts were made to obtain fine, cubic zirconia powders (yittria stabilized zirconia), and using simple and cost-effective chemical method via modified sol-gel process with new organic precursors. The Zr: Sucrose ratio, effective in particle size, has been optimized.

Experimental

$ZrCl_4$ & Y $(NO_3)_3.6H_2O$ were calculated for the final composition of 8% mol YSZ. The salts were dissolved in deionized water and heated to 90 °C on hot-plate. The Sucrose: pectin mixture with the mass ratio of 1:0.02 was added drop wise to the precursor, under continuous stirring, to prevent agglomeration. Four Samples were made by this procedure to optimize the molar ratio of Zr: Sucrose shown in table 1. The thermal treatment continues for 2 hours until the mixture becomes completely gelatinized and the xerogel is formed. This xerogel taken the appearance of a brown resin is subjected to thermal treatment to transform into YSZ nanoparticles [5].

Table1. Molar ratio of Zr: Sucrose

sample	A	B	C	D
Zirconium	1	1	1	2
Sucrose	2	4	10	100

Results & discussion

In the sucrose and pectin mixture, pectin forms a polymer matrix in which the metal cations are distributed and sucrose acts as a strong chelating agent. Thus, metallic ions (e.g. Zr^{4+}) are bound by the sucrose molecule and the resulting complex molecule is trapped between pectin layers. The chelated complex mass is obtained by polymerization via gel formation and the final particles are obtained upon decomposition in the calcination process. During heating, the metal ion complex is decomposed into CO_2 and H_2O. Since all these products are gaseous, they prevent agglomeration [6].

The XRD diffraction patterns (2θ between 20 and 80°) showed that the obtained nanoparticles are stable in cubic crystal form. To observe any trace of tetragonal phase Raman data was performed.

Results of the grain size analysis using Scherrer formula applied on the first peak of the obtained XRD pattern showed samples have nanocrystal size. According to the size obtained, the Zr: sucrose ratio has reverse relation with nanocrystal size.

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MFC —Wastewater Treatment

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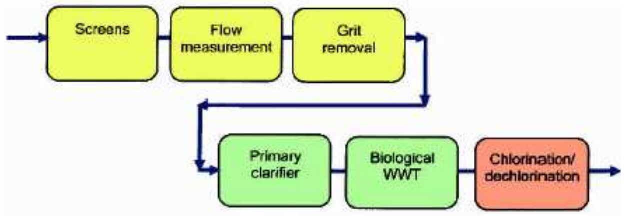
Introduction

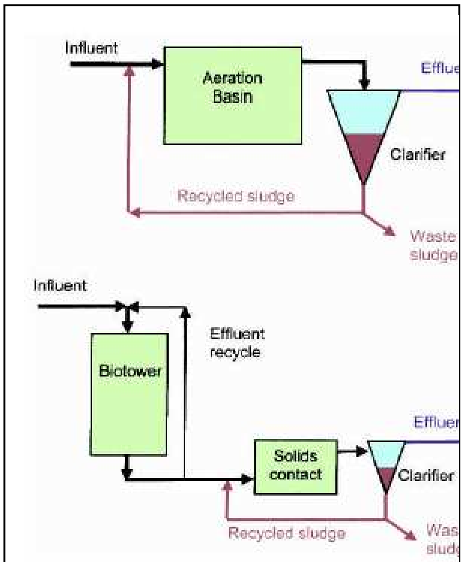
A microbial fuel cell (MFC) is a bioreactor that converts chemical energy in the chemical bonds in organic compounds to electrical energy through catalytic reactions of microorganisms under anaerobic conditions. It has been known for many years that it is possible to generate electricity directly by using bacteria to break down organic substrates. The recent energy crisis has reinvigorated interests in MFCs among academic researchers as a way to generate electric power or hydrogen from biomass without a net carbon emission into the ecosystem. MFCs can also be used in wastewater treatment facilities to break down organic matters. They have also been studied for applications as biosensors such as sensors for biological oxygen demand monitoring. Power output and Coulombic efficiency are significantly affected by the types of microbe in the anodic chamber of an MFC, configuration of the MFC and operating conditions. Currently, real-world applications of MFCs are limited because of their low power density level of several thousand mW/m^2. Efforts are being made to improve the performance and reduce the construction and operating costs of MFCs.

A typical wastewater treatment process (WWTP) treating domestic wastewater consists of a series of unit processes all designed with specific functions to make the monitoring and treatment of the wastewater as efficient as possible.

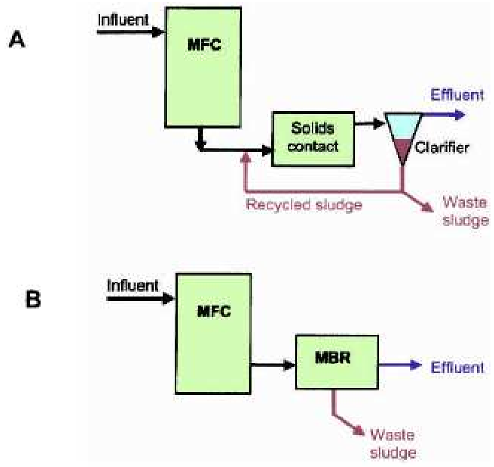
Please consider and compare these three well-known methods for WWTP:



Process flow train for a typical domestic wastewater treatment plant in the USA



Biological treatment process consisting of a bioreactor and secondary clarifier.(A) Activated sludge process with aeration basin, sludge recycle, and waste sludge lines; (B) Trickling filter process consisting of biotower, solids



Flow diagrams for using an MFC reactor as the biological treatment process. (A) A conventional treatment train with a downstream solids contact tank, sludge recycles line, and clarifier. (B) Combined with a MBR using the MFC as a pretreatment method to provide power for the MBR reactor. In a third option, the MFC could become a type of MBR (not shown).

Result & Discussion

The MFCs were considered to be used for treating waste water early in 1991 (Habermann and Pommer, 1991). Municipal wastewater contains a multitude of organic compounds that can fuel MFCs. The amount of power generated by MFCs in the wastewater treatment process can potentially halve the electricity needed in a Conventional treatment process that consumes a lot of electric power aerating activated sludge. MFCs yield 50–90% less solids to be disposed of (Holzman, 2005). Furthermore; organic molecules such as acetate, propionate, and butyrate can be thoroughly broken down to CO_2 and H_2O. A hybrid incorporating both electrophiles and anodophiles are especially suitable for wastewater treatment because more organics can be biodegraded by a variety of organics. MFCs using certain microbes have a special ability to remove sulfides as required in wastewater treatment (Rabaey et al., 2006). MFCs can enhance the growth of bioelectrochemically active microbes during wastewater treatment thus they have good operational stabilities. Continuous flow and single-compartment MFCs and membrane-less MFCs are favored for wastewater treatment due to concerns in scale-up (Jang et al., 2004; Moon et al., 2005; He et al., 2005). Numerous fuel cells have been shown to generate power by oxidation of compounds found in wastewater streams (e.g. Gil et al., 2003; Rabaey et al., 2004; Liu and Logan, 2004). Two useful purposes can be realized by this procedure: (a) for the removal of the organic compounds from the waste stream and (b) for the generation of electrical power. A recent review on the subject calculates that the wastewater from a town of 150,000 people could potentially be used to generate up to 2.3MWof power (assuming 100% efficiency), although a power of 0.5MW might be more realistic. It should be mentioned in this context that up to 80% of the chemical oxygen demand of wastewater can be removed by treatment in a microbial fuel cell and it is possible that the electricity generated in this manner could be used on site to power further treatment of the wastewater. An economic study within the review (Logan, 2005) shows the potential for this application, although this is highly dependent on local power costs.

Conclusion

The success of specific MFC applications in wastewater treatment will depend on the concentration and biodegradability of the organic matter in the influent, the wastewater temperature, and the absence of toxic chemicals. Materials costs will be a large factor in the total reactor costs. Mainly anodic materials commonly used in MFC reactors, such as graphite foams, reticulated vitreous carbon, graphite, and others, are quite expensive. Simplified electrodes, such as carbon fibers, may alleviate these electrode costs. The use of expensive catalysts for the cathode must also be avoided. Another crucial aspect is the removal of non-carbon based substrates from the waste streams: nitrogen, sulfur, and phosphorus containing compounds often cannot be discharged into the environment at influent concentrations. Similarly, even particulate organic compounds will need to be removed and converted to easily biodegradable compounds, as part of an effective wastewater treatment operation. As aforementioned, MFCs can potentially be used for different applications. When used in wastewater treatment, a large surface area is needed for biofilm to build up on the anode. A breakthrough is needed in creating inexpensive electrodes that resist fouling. It is unrealistic to expect that the power density output from an MFC to match that of conventional chemical fuel cell such as a hydrogen-powered fuel cell. The fuel in an MFC is often a rather dilute biomass (as in wastewater treatment) in the anodic chamber that has a limited energy (reflected by its BOD). Another limitation is the inherent naturally low catalytic rate of the microbes. Even at their fastest growth rate microbes are relatively slow transformers. Although Coulombic efficiency over 90% has been achieved in some cases, it has little effect on the crucial problem of low reaction rate. Although some basic knowledge has been gained in MFC research, there is still a lot to be learned in the scale up of MFC for large-scale applications.

Nanotechnology in Fuel Cells

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There are several uses of nano materials; one of the considerable fields of nanotechnology is its uses in fuel cells. Fuel cells are promising alternatives to present power sources. In the large field of nanotechnology, polymer matrix based nano composites have become a prominent, one of the areas include polymer-based are fuel cells. Nano particles of platinum reduce the amount of platinum needed as electrode, or using nano particles of other materials to replace platinum entirely and thereby lower costs. Fuel cells contain membranes. Nanotechnology creates more efficient membranes. The effect of the large surfaces or interfaces of nano-sized carbon is important in nanotechnology treatment. The carbon nano fiber formation by polymer blend technology is progressing. We are now applying carbon nano fibers polymer composites as a candidate bipolar plate in fuel cells, utilizing the high modulus and high strength. A novel metallic porous medium with improved thermal and electrical conductivities and controllable porosity was developed based on micro/nano technology for its potential application in fuel cells. The small thickness and straight-pore feature of the novel material provides improved water management even at low flow rates. In this paper we try to introduce some aspects of nanotechnology used in fuel cells.

Keywords: *Fuel cell, Nanotechnology, Membrane, Catalyst*

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Production of polymeric nanocomposite Bipolar Plate for PEM and DMFC fuel cells

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The polymer electrolyte membrane fuel cells(PEM and DMFC) are the most promising power sources for stationary and transportation application in the future due to many attractive features. These features include high efficiency, high power density, relative low operating temperature, conventional fuel supply and long life time. In order to make the PEM and DMFC fuel cells more economically feasible, processing and material costs need to be reduced. In a fuel cell stack, the electrically conductive plates are often referred to as bipolar plates because one face contacts the cathode electrode while the opposite face contacts the anode electrode. Each bipolar plate therefore conducts electrical current from anode of one cell to the cathode of the adjacent cell in the stack. Bipolar Plate is a vital component of PEM and DMFC fuel cells, which supplies fuel and oxidant to reactive sites, removes reaction products, collects produced current and provides mechanical support for the cells in the stack. Bipolar Plates constitute more than 60% of the weight and 30% of the total cost in a fuel cell stack.one approach to reduce the cost of fuel cells bipolar plates is to use of polymeric nanocomposite bipolar plate instead of graphite or metallic bipolar plates that exhibits adequate conductivity (about 20 mohm.cm^2 which is well within an acceptable level (i, e. not greater than about 100 to 200 mohm.cm^2)), corrosion resistant, low manufacturing costs and good mechanical strength. In this work we use polypropylene thermoplastic (resin base) and Multiwall carbon nanotube and graphite (additive) for preparation of polymeric nanocomposite that have good electrical conductivity (>10 s/cm), high mechanical

Strength and low cost. The impact of different types of fillers on the composite blend properties was evaluated, as well as the synergetic and electrical conductivity effect of mixtures of filler types and concentrations within a thermoplastic polymer matrix. Research results show that Nanocomposite with loading up to 15% Multiwall carbon nanotube and 45% graphite exhibit better performance.

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Synthesis of PANI-DBSA/multi-wall carbon nanotube/polymer nanocomposite for fabrication of bipolar plate in PEM fuel cell

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Abstract

Conducting polymers are finding increasing number of applications in various electronic devices such as chemical sensors, light diodes, etc. High molecular weight of polyaniline (PANI) has emerged as one of the most promising conduction polymer. Compared with other conducting polymers, PANI has significant importance because it exhibits good environmental stability, ease of prcessability and high conductivity especially a simple and reversible acid/base doping/de-doping chemical property. But its main disadvantages are poor thermal stability and poor processabilty both in melt and solution due to its stiffness of the backbone. The overcoming of these disadvantages was however possible due to the counter-ion inducing to the PANI's backbone, which can be achieved by doping PANI with functional protonic acids, such as dodecylbenzenesulfonic acid(DBSA).

Recent studies have shown that, besides possibly improving the mechnical and electrical properties of polymers, the formation of polymer/CNT composites is considered as a capable approach for an incorporation of CNTs into polymer-based devices. Among these polymer/CNT composite, many reports have focused on the combination of CNT conducting polymers. Among various cinducting polyers, polyaniline(PANI) hs a potential use in synthesizing polymer/CNT composites due to its good processability, environmental stability and revesible control of conductivity both charge-transfer doping and protonation. Significant progress has been made in fabricating PANI/multi-walled carbon nanotube (MWNT), the doped

PANI/MWNT composite with or without protonic acid synthesized by in situ polymerization.

A significant part of the PEMFC fuel cell stack is the bipolar plates (BPs), which account for about 80% of total weight and 45% of stack cost. They are designed to accomplish many functions, such as distribute reactants uniformly over the active areas, remove heat from the active areas, carry current from cell to cell and prevent leakage of reactants and coolant. Furthermore, the plates must be of inexpensive, lightweight materials and must be easily manufactured. The BPs have the following functions to perform: a) to distribute the fuel and oxidant within the cell b) to facilitated water management within the cell d) to separate individual cells in the stack e) to carry current away from the cell and f) to facilitate heat management. Hence, the materials that BPs is made of would have different physical and chemical properties related to each function.

In this work, we describe the synthesis and characterization of PANI-DBSA with MWNTs fabricated by in situ polymerization. In order to improve the MWNT-PANI-DBSA interface, chemical fictionalization of the MWNT is used to increase the interfacing binding between the MWNT and PANI. Thus polyethylene(PE) and polypropylene(PP)/ MWNT-PANI-DBSA nanocomposite were prepared through mixing polymer solution with MWNT-PANI-DBSA in toluene solvent by ultrasonic bath. The results of this study clearly show that prepared nanocomposite have suitable distribute and high conductivity, thus it is suitable for fabrication of bipolar plate in fuel cell.

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Disadvantage of Fuel Cells

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Fuel cells have several important advantages over conventional electrical energy generation from sources such as fossil fuels. Although, this relatively developing technology have several problems, that should be solved. In addition to technological problems, such as high costs, several changing the materials, fuel reforming, long start up time, degradation over time, low voltage, source of materials, special catalyst, some environmental problems may be created by growing this technology. In this paper we hope to introduce and discuss several aspects of disadvantages of fuel cells.

Keywords: *Fuel cell, Disadvantage, Environmental*

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Methanol oxidation on titanium supported nickel

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Electrochemical oxidation of methanol on platinum and platinum-based catalysts has been extensively examined. It is well-known that nickel and some Ni-based materials exhibit attractive activity for the electrochemical oxidation of some organic molecules like methanol, ethanol, cyclohexanol, glucose and aspirin. The titanium is a hard metal. It is corrosion resistant, has a high mechanical strength, a reasonable cost, wide electrochemical potential windows and good stability. Because of its excellent properties, titanium has been applied as a substrate in order to prepare novel and stable electrocatalysts including the well-known DSA (RuO2–TiO2/Ti) electrode. All solutions were prepared with doubly distilled water. All electrochemical experiments were performed in a conventional three-electrode cell powered by an electrochemical system comprised of an Autolab PGSTAT30 potentiostat/galvanostat and FRA2 boards (Eco Chemie, Utrecht, The Netherlands). The system was run by a PC through FRA and GPES 4.9 software. The working electrode was the Ni/Ti the counter electrode was large Pt foils. Saturated calomel electrode (SCE) was used as the reference. In this work, the electroactivity of Ni/Ti catalyst for the methanol oxidation in alkaline solutions was accessed by electrochemical voltammetric techniques. Effect of methanol concentrations on CVs of Ni/Ti with the potential sweep rate of 10 mV/s was investigated and results are shown in Fig. 1. Methanol concentrations (C_{CH3OH}) were changed from 0 to 0.5 M indicated by the lines a–d, respectively. The anodic currents increase with the C_{CH3OH} at potentials higher than 0.37 V,revealing the electrocatalytic activity of the Ni/Ti for methanol oxidation. Conversely, cathodic currents corresponding to the reduction of NiOOH decrease with C_{CH3OH}. In addition, the cathodic peak potentials shift to more positive with C_{CH3OH}. This results from the consumption of NiOOH caused by the presence of methanol through reaction. As a conclusion the electrocatalytic activity of the Ni/Ti electrode for methanol oxidation was evaluated by electrochemical voltammograms, The Ni/Ti showed extremely higher currents and lower onset potentials of methanol oxidation than the pureNi.

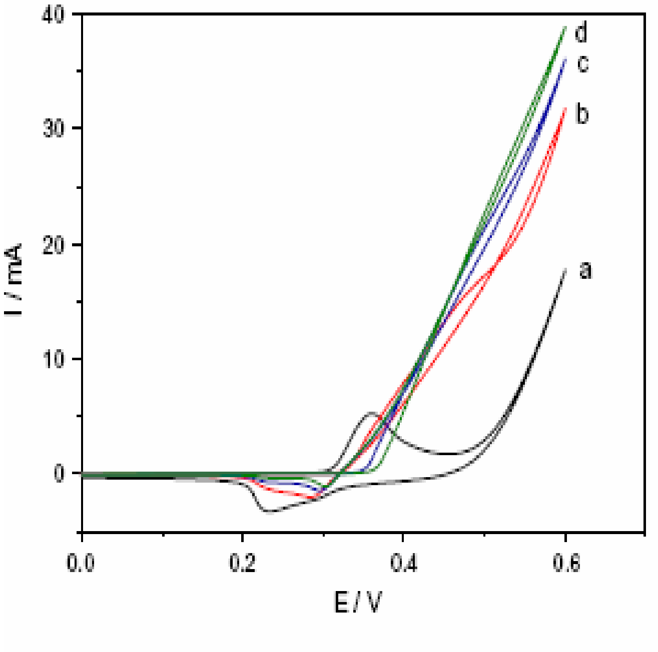

Fig. 1. Cyclic Voltammograms of the Ni/Ti electrode from 0 to 0.6 V at the scan rate of 10 mV/s in 1 M NaOH solution with the various concentrations of methanol:0 M (a), 0.1 M (b), 0.25 M (c), and 0.5 M (d). 19

Nickel as a catalyst for the electro-oxidation of 2-propanol in alkaline medium

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Introduction

In the recent years a great deal of interest exists for finding a suitable electrocatalyst in alcohol fuel cell have both high efficiency and low price. The electrocatalytic oxidation of MeOH, EtOH on electrodes such as Pt, Pd, Au, Ni have been reported. But Ni recently has been more interested due to its low price and good efficiency [1].

In this work we focuses on the electrochemical oxidation of 2-propanol on nickel in the alkaline solution.

Experimental

Sodium hydroxide, 2-propanol used in this work was analytical grade of Merck origin. Cyclic voltammetry experiment was done in a conventional three electrode cell. A nickel rod was used as a working electrode. All potentials were refreed to the saturated Ag/AgCl electrode which was used as a reference electrode through this work. A graphite rod was employed as a counter electrode. Cyclic voltammetric measurements were obtained using a potentiostat/Galvanostat model EG/G 273A.

Results and disscusion

In the cyclic voltammetry experiment polarization was started by potential scanning at a scan rate of 10 mVs^{-1} from 0 to 600 mV. The cyclic voltammetric behavior of massive nickel electrode in 1 M NaOH solution has been shown shown in the below figure by (a) voltammogram. By scanning the potential from 0 to the positive values, a anodic peak appeared in 0.49 V and in the reverse scan, a cathodic peak was observed in 0.43 V that related to redox species of Ni^{+2} / Ni^{+3} [2].

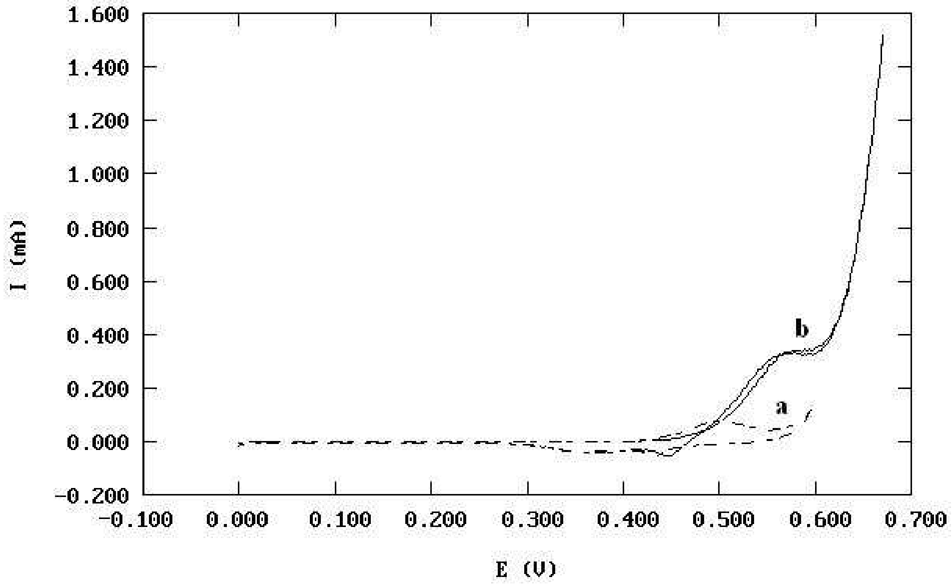

Fig 1. Cyclic voltammograms of Ni electrod in the absence (a) and the presence (b) of 2-propanol in 1.0 M NaOH at a scan rate of 10 mVs^{-1}.

By adding 2-propanol to the solution a new anodic peak was obtained in 560 mV that is concerned to the electro-oxidation of 2-propanol that has been remarked in (b) voltammogram. As we consider by adding 2-propanol to the alkaline medium the anodic peak current rise to 0.343 mA and a decrease in the cathodic peak is observable too.

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ELECTRO OXIDATION OF ETHANOL ON COPPER AND NICKEL ELECTRODES BY CYCLIC VOLTAMMETRY

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Fuel cells are being considered as an important technology that can be used for various power applications. All electrochemical experiments were performed in a conventional three-electrode cell powered by an electrochemical system comprised of an Autolab PGSTAT30 potentiostat/galvanostat and FRA2 boards (Eco Chemie, Utrecht, The Netherlands). The system was run by a PC through FRA and GPES 4.9 software. KOH was used as the supporting electrolyte. The aim of this work is to study the electro oxidation of ethanol on copper and nickel electrodes by cyclic voltammetry (CV). The effect of ethanol concentration may cause the increase of current density and shift ethanol oxidation potential peak (A4 peaks in Figure 1) up to more positive potential. Figure 2 shows the effect of ethanol concentration to current density. Figure 2 shows the peak current density increased with increasing of ethanol concentration. As a conclusion, it can be said that Cu electrode was a better electrode compared with Ni electrode for electro oxidation of ethanol using CV method, however it was observed that Cu electrode was easily oxidized by the formation of metal oxide on the electrode surface compared with Ni electrode.

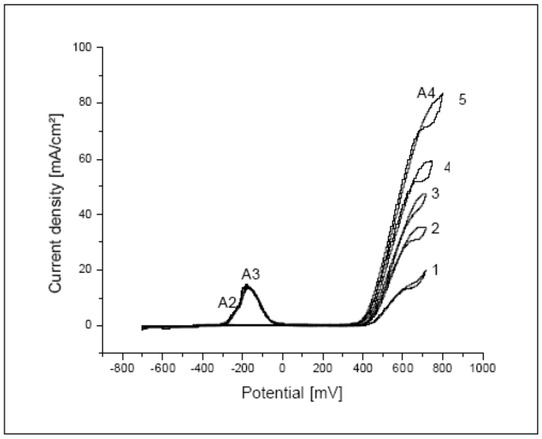

Figure 1: Cyclic voltammograms for Cu electrode in(1) 1% (2) 2% (3) 3% (4) 4% and (5) 5% (v/v) ethanol +1.0 M KOH. Anodic sweep from –700 mV to +700 mV (vs. SCE).Scan rate 10 mVs-1

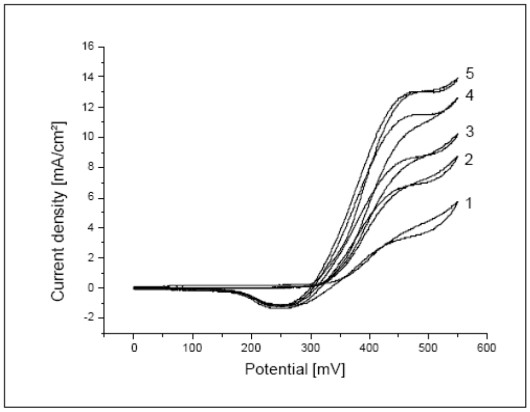

Figure2: Cyclic voltammograms for Ni electrode in: (1) 1% (2) 2% (3) 3% (4) 4% and (5) 5% (v/v) ethanol + 1.0 M KOH. Sweep scan from 0 mV to 550 mV (vs. SCE). Scan rate mVs-1

The investigation of kinetic mechanism of hydrogen evolution reaction on Hg and HgCu alloy

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Introduction

With the intention of improving the utilization of the electrolytic hydrogen production process, many attempts have been made to develop efficient and durable electrocatalysts for the hydrogen evolution reaction (HER) in alkaline solutions. The catalytic activity for hydrogen evolution can be enhanced by the modification of the electronic structure of electrode metals by alloying or by the use of some suitable preparation method which allows obtaining electrodes with highly developed rough or porous surfaces [1].

The purpose of the present work is to investigation of the kinetic and mechanism of hydrogen evolution reaction on HgCu alloy and also study underpotential deposition of hydrogen on these electrode.

Keywords: *Hydrogen evolution, Mercury, Copper, Alloy.*

Experimental

Sulfuric acid used in this work was Merck products of analytical grade and was used without further purifications. Electrochemical studies were carried out in a conventional three electrode cell powered by an electrochemical system comprising of EG&G model 273 potentiostat/galvanostat. The system is run by a PC through M270 commercial softwares via a GPIB interface. The HgCu alloy is prepared by constant current deposition of Cu on Hg electrode from copper solution.

Results

Fig. 1 shows the Nyquist diagrams of HgCu electrode in 0.1M H_2SO_4 in different copper concentration with (1) 0, (2) 20s, (3) 30s, (4) 40s deposition on Hg for alloy formation recorded at the reduction peak potential as dc-offset for hydrogen.

The Nyquist diagrams consisted of two slightly depressed strongly overlapping capacitive semicircles in the high and low frequency sides of the spectrum. The depressed semicircle in high frequency can be related to the combination of charge transfer resistance and the double layer capacitance.The low frequency semicircle was attributed to the adsorption of hydrogen on the electrode surface.

The reaction resistance of the impedance spectra for HgCu alloy prepared in 40s is less than Hg electrode and the two other alloys.

The mechanism of hydrogen evolution reaction on HgCu electrode is:

$$H_3O^+ + M + e \xleftrightarrow{k_1', k_{-1}'} MH_{ad} + H_2O$$

$$MH_{ad} + H_3O^+ + e \xleftrightarrow{k_2', k_{-2}'} M + H_2 + H_2O$$

$$MH_{ad} + MH_{ad} \xleftrightarrow{k_3', k_{-3}'} 2M + H_2$$

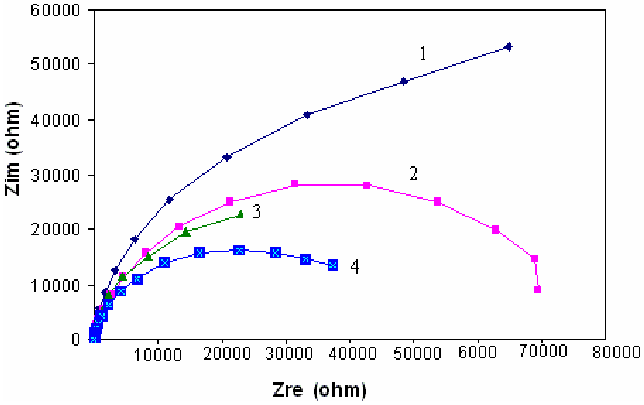

Fig.1.

1. Hg
2. HgCu 20s deposition
3. HgCu 30s deposition
4. HgCu 40s deposition

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predict the maximum efficiency of the PEM fuel cell

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Abstract

The maximum efficiency of the PEM fuel cell And the reversible voltage for the hydrogen/oxygen reaction used in the fuel cell with porous electrode is investiget in this work. This is the maximum voltage possible given consideration of the second law of thermodynamics. the maximum efficiency of a hydrogen/oxygen fuel cell is approximately 83% efficient at 25 °C. There are three contributors to the irreversibility of energy conversion in a fuel cell, and they are ohmic losses , mass transport losses , and limitations in the kinetics of the reaction or activation losses (the rate of electrocatalysis is finite, which is especially true at the cathode in a PEM fuel cell). In actual operation, these irreversibilities cause the fuel cell to be substantially less efficient than the efficiency predicted.

Introduction

The depleting fossil fuel resources and increasing pollution are leading to the research and development of alternate energy generation techniques like fuel cells and solar cells. Fuel cell (FC) systems have a high efficiency and use easily available hydrocarbons like methane thus alleviating the fuel shortage. Moreover, since the by-product is water, they have a very low environmental impact. The fuel cell system consists of several subsystems and a lot of effort in diverse areas is required to make it a popular choice for power generation. Fuel cells have been used extensively and successfully in spacecrafts and now efforts are on to commercialize the fuel cell. They have a wide range of applications .which are

Power generating stations, Auxiliary units, Buses and cars, Portable electronics, Cellular phones [1].

Fuel cells are categorized based on the type of electrolyte used. Alkaline FC, Proton exchange membrane FC , Phosphoric acid FC, Molten carbonate FC, Solid oxide FC are Some of the popular fuel cells .Proton Exchange Membrane fuel cells (PEMFCs) have, within the past decade, become the focus of much interest in engineering because of their potential to make electrical power production more "green": that is, environmentally responsible. Because of the commercial availability of mass-produced fuel cell components, the concept of using fuel cells on a large scale to help supply grid electrical power, or for use in automobiles, is becoming closer to a reality every day[2].

In order to make fuel cells more attractive, much effort has been made to either increase the performance and efficiency of PEMFC components, or to decrease their costs, or both. Much of the work during the mid- to late- 1990's on PEM fuel cells was aimed at the MEAS[3,4].

In this work investigate the maximum efficiency of the PEM fuel cell with the second law of thermodynamics. With calculated the free energy of gibs and

Enthalpy and chemical reaction in the fuel cells, the maximum efficiency of a hydrogen/oxygen fuel cell is approximately 83% efficient at 25 °C.

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Fuel Cell Membranes

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One of the most important pillars of fuel cells is design of proper membrane for exchange of substances between two electrodes. Various aspects of membranes were investigated, such as: structural and thermal properties, proton conductivity, pore characteristics, hydrogen permeability, elastic modulus, mechanical and thermal stability and performance in fuel cell tests. Various membranes have been used in fuel cells, for example: proton exchange membrane, glass composite membrane, polymer electrolyte membrane, nano composite membranes, hydrocarbon membrane, clay modified with silane, proton conducting membrane used in fuel cells. Each membrane is designed for specific propose, and has advantages and disadvantages. In this paper we would like to introduce structure, advantages and disadvantages of fuel cell membranes.

Keywords: Fuel cell, Membrane

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MFC — Today and Future

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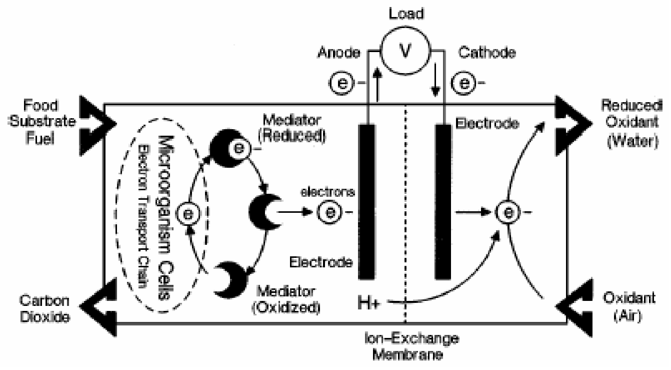
Introduction

With the increasing concern for alternative energy sources, waste management, global climate change, and non-edible feedstocks, the search for novel technological solutions continues. Fuel cells are one alternative energy technology being studied for full-scale implementation (R.A.Bullen et al., 2006). These can be classified into three subgroups: catalytic, enzymatic, and microbial. Since the turn of the century, the research on microbial fuel cells (MFCs) has experienced rapid increases. MFCs are unique in their ability to utilize microorganisms, rather than an enzyme or inorganic molecule, as catalysts for converting the chemical energy of feedstock directly into electricity. Within this article, a brief description will firstly be given of the history of biofuel cells together with coverage of some of the major historical advances; finally we will discuss some of the proposed uses of biofuel cells together with a short consideration of future research possibilities and applications of these systems.

Result & Discussion

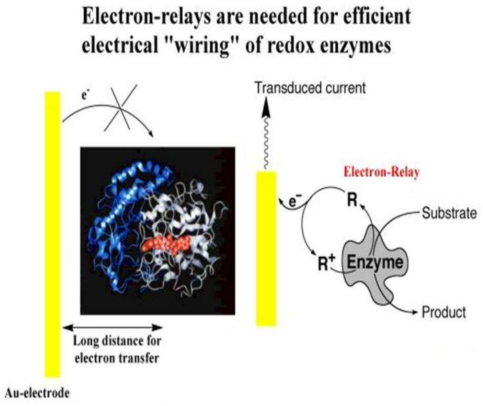
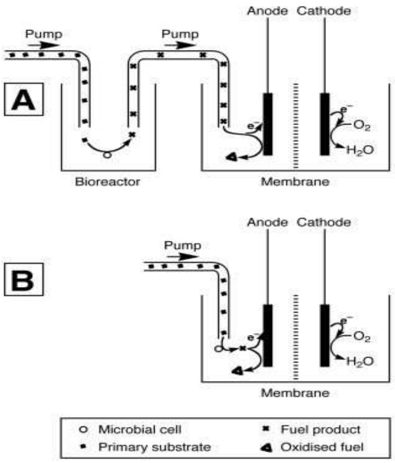
While the concept of bioelectricity generation was first demonstrated nearly a century ago, MFCs as we now know them from recent work really need to be considered as a new technology. Biofuel cells conducted with yeast and bacteria that needed chemical mediators to be added to the reactor were very unlikely to have practical applications. Thus, modem MFCs can be considered to have only emerged in 1999 with the finding of electricity generation without the need for exogenous mediators (Kim et al., 1999) Since then, substantial progress has been made in the field despite the fact that only a relatively few research laboratories have been working in this area. We can expect that as more researchers engage in improving MFC technologies that advances will be made even more quickly. In the past 8 years, we have seen a nearly logarithmic increase in power production with MFCs using oxygen at the cathode. Before 2001, power production was less than 0.1 W/m^2 of electrode. In 2001 several reports emerged on systems with power over 10 mW/m^2 (normalized to anode surface area), and in recent years we have seen power levels over 1000 mW/m^2, with a maximum value achieved of 2400 mW/m^2 (normalized to the cathode surface area) (Logan et al., 2007). This is still at least an order of magnitude below power densities that could theoretically be achieved before mass transfer to the biofilm would limit power densities. Our attention is now shifting from power normalized to electrode surface area, to power per volume. This transition reflects a growing appreciation by engineers that this technology is ready to emerge into practical applications. Most early MFC studies were not conducted to optimize volumetric power density but rather to explore materials and understand factors that limited power on an area basis. As systems have been designed more with a desire to improve performance on the basis of reactor volume, power volumetric power densities have increased for MFCs using oxygen at the cathode, from values below 1 W/m^3 only a few years ago to 115 W/m^3 today (Cheng and Logan 2007 ; Logan and Regan 2006). We can expect these power densities to continue to increase in the next few years. It has been suggested that a goal for MFCs is to reach a power volumetric density comparable to that produced with anaerobic digesters (Rabaey and Verstraete 2005), or -400 W/m^3. While that is a reasonable goal, hydraulic retention times, energy used for pumping and materials costs all we need to be included in this analysis. A goal for MFCs described in is to achieve HRT comparable to that used for an activated sludge reactor, or an HRT of about 4-6 hours. Anaerobic digesters used for sludge treatment can have detention times of a month or more, and thus are impractical for treatment of dilute streams such as those typical of domestic wastewater treatment plants and many industrial wastewaters. The real goal of an MFC design will be one that is economical on the basis of capital and operational costs compared to that needed for conventional designs.

Biological fuel cells are a potential green energy technology. In a microbial fuel cell bacteria do not directly transfer the electrons which they produce to their characteristic terminal electron acceptor; instead, these electrons are diverted toward an electrode (anode). The electrons are subsequently conducted over a resistance or power user toward a cathode, and thus, bacterial energy is directly converted to electrical energy (Rao, J. R. et al 1976). Three main types of biofuel cells can be distinguished: photoautotrophic-type biofuel cells (Tsujimura, S. et al., 2001), cells which combine the utilization of photochemically active systems and biological moieties to harvest the energy from sunlight and convert this into electrical energy; more common heterotrophic- type biofuel cells (Cooney, M. J. et al.,1996), cells which generate electricity directly from an organic fuel such as glucose, using either enzymes or complete microorganisms; and sediment biofuel cells (Bond, D. R et al.,2002), cells which use a primary fuel (usually an organic waste such as corn husks) and generate a material such as hydrogen, which is then used as a secondary fuel within a conventional hydrogen/oxygen fuel cell. Biofuel cells have some characteristics that are similar to those of traditional power sources, as well as to those of anaerobic reactors. There are several potential uses of biofuel cells: Transport



and energy generation (electricity generation), Implantable power sources (Biohydrogen), Wastewater treatment and Robots (Biosensor).

Trend in biofuel cell development:

 Enzymatic biofuel cell • Membraneless biofuel cells • ”Wiring”of redox centers of enzymes • Miniaturisation • Carbon nanotubes and porous carbon as enzyme matrix	 Microbial-based biofuel cell • Immobilized mediator • Mediatorfree cells • Mixed microbial community –sewage sludges • Carbohydrate, alcohols, cysteine, acetate

Conclusion

The development of biofuel cells for practical applications is a field which is still in its infancy, although there is unquestionably much potential for further improvement. Biofuel cells offer several possible advantages over existing technologies, such as the use of lithium–iodine batteries in implantable devices such as heart pacemakers. Ideally an implanted biofuel cell would use a biological metabolite fuel source such as glucose or lactate, both of which are readily available in physiological fluids such as blood. The high turnover of a “wired” enzyme electrode in such applications could generate power levels capable of meeting the needs of many devices without the need for a mediator. There are a number of problems which need to be addressed, however, the most important of which is that most of the enzyme modified electrodes described in the literature to date have lifetimes in the order of weeks whereas for in vivo implanted devices, longevities of years would be required for practical application. Unfortunately most of the biofuel cells described today would be capable of meeting demands for biomedical devices implanted for short term application only. Although the stabilization of enzymes has been an active area for many years, the state-of-the-art is not capable of meeting the requirements of such devices (Barton et al., 2004). It is probable that enzymes will have to be modified by routes such as genetic engineering if the required enzyme stabilities are to be met. A second problem that must be addressed is that of biocompatibility; the biofuel cell must be capable of existing in the physiological environment without an unacceptable degree of biofouling occurring over extended periods of time which otherwise would lead to fouling of the device or to physiological harm to the patient. Other possibilities for biofuel cell research include the future development of power supplies for use in remote areas. In an ideal scenario biofuel cells such as these should be capable of using readily available fuel sources. Plant saps, for example, often contain high levels of sugars which could be used as a fuel. Many conventional hydrogen or alcohol fuel cells require expensive noble metal catalysts and moreover often require extreme conditions of pH or high temperature. Biological fuel cells which usually perform optimally at near ambient temperatures and neutral pH clearly would offer benefits in this respect. Microbial fuel cells may also in the future be used to help degrade organic waste such as sewage sludge whilst also producing electricity as a useful by-product. Although some specialist devices for providing, for example, short lifetime implantable power devices could now be considered feasible, it is obvious that a continuing research effort needs to be made before we will see large scale use of biofuel cells. Problems of lifetime, stability and power density all need to be addressed, although the possible benefits of this technology are likely to drive continuing research. We need to improve our knowledge of biocatalysis, electron processes at surfaces, biological and other material stability to realize this vision.

Electrooxidation of ethanol on a nickel oxyhydroxide-modified electrode

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In the past decades, the direct methanol fuel cell (DMFC) has drawn attention for its simple construction with reduced dimensions and high-energy efficiency. Progress has been made in this field [1-3]. However, the intrinsic DMFC disadvantage is the toxicity of methanol. Therefore, researchers have looked for other small alcohol molecules as alternative fuels. Ethanol has emerged as the first choice because of its relative non-toxicity and low volatility together with a higher energy density compared to methanol (8.01 KWh kg^{-1} versus 6.09 KWh kg^{-1}). Other important considerations for choosing ethanol are its low price, natural availability, renewability, high power density, zero green-house contribution to the atmosphere and its transportability. Among the published reports on proton exchange membrane fuel cells (PEMFC) with alcohols as fuel, the direct ethanol fuel cell (DEFC) seems promising, especially for the application in devices like electric vehicles, mobile telephones and laptops. Pt and Pt alloy electrodes provide simple electrocatalytic surface for oxidation of ethanol. However, the complete oxidation of ethanol in DEFC remains the crux of the matter, because, unlike the case of DMFC, it is necessary to break the C-C bond of ethanol at low temperatures.

The purpose of the present work is to study the electrochemical oxidation of ethanol on a nickel modified NiOOH electrode in room temperature in basic solution.

Sodium hydroxide and ethanol used in this work were Merck products of analytical grade and were used without further purifications. Doubly distilled water was used throughout.

Electrochemical studies were carried out in a conventional three electrode cell powered by an electrochemical system comprising of EG&G model 273 potentiostat/galvanostat. The system is run by a PC through M270 commercial softwares via a GPIB interface. A dual Sat’d Ag/AgCl, a Pt wire and a nickel disk electrode were used as the reference, counter and working electrodes, respectively. All studies were carried out at 298± 2 K.

The nickel oxide film was formed electrochemically on nickel electrode in a regime of cyclic voltammetry and tested for electrooxidation of ethanol in alkaline media. The modified electrode showed electrocatalytic activity for the oxidation of ethanol at around 600 mV/Ag,AgCl. The Ni modified glassy carbon electrode exhibited large response current for oxidation of ethanol. A kinetic model was developed and using the methods of cyclic voltammetry and choronoamperometry the kinetic parameters such as transfer coefficient (α), the catalytic reaction rate constants (k), and the diffusion coefficient of ethanol in the bulk of solution were determined.

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Electrocatalytic oxidation of methanol on Ni and NiCu alloy modified glassy carbon electrode

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1. Introduction

The direct methanol fuel cell (DMFC) has recently received a good deal of attention for both mobile and stationary applications [1,2]. Methanol as fuel has been numerous advantages such as simple operation and ease of fuel storage and distribution. However, compared to the hydrogen based fuel cells, DMFC still remains to be further developed. Different electrode materials were used as a catalyst for the electro-chemical oxidation of methanol such as, Pt-Ru and Pt-Ru-P/carbon nano-composites [3], Pt/Ni and Pt/Ru/Ni alloy nano-particles [4]. The use of alkaline solutions in a fuel cell has many advantages such as increasing its efficiency [5,6], a wider selection of possible electrode materials, a higher efficiency of both anodic and cathodic processes, almost no sensitivity to the surface structure [7] and negligible poisoning effects in alkaline solutions were observed [8,9]. The purpose of the present work is to study the electrochemical oxidation of methanol on a nickel and Nickel-copper alloy modified glassy carbon electrode in a solution of 1 M NaOH.

2. Experimental

Electrochemical studies were carried out in a conventional three electrode cell powered by an electrochemical system comprising of EG&G model 273 potentiostat/galvanostat. The system is run by a PC through M270 commercial softwares via a GPIB interface. A glassy carbon (GC) disk electrode, a Pt wire, and Ag/AgCl-Sat'd KCl were employed as working, counter and reference electrodes, respectively. All studies were carried out at 298± 2 K. Films of nickel were formed on the GC surface by galvanostatic deposition.

3. Results and discussion

Fig. 1 shows cyclic voltammograms of GC/Ni and GC/NiCu electrode in 1M NaOH solution in the presence of 0.3 M methanol at a potential sweep rate of $10 mVs^{-1}$. As can be seen in 0.3 M methanol GC/NiCu electrode generates higher current density for electrooxidation in NaOH solution due to higher surface concentration of β-NiOOH form.

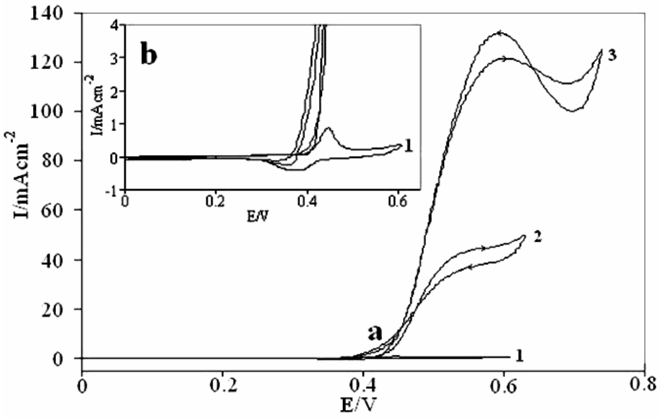

Fig. 1. Cyclic voltammograms in the absence (1) and the presence of 0.3 M of methanol on (2) GC/Ni and (3) GC/NiCu electrode in 1M NaOH solution. Potential sweep rate was $10 mVs^{-1}$. (b) Initial potential of methanol oxidation.

4. Conclusion

The nickel oxide film was formed electrochemically on electrodeposited nickel and nickel-copper alloy in a regime of cyclic voltammetry on a glassy carbon electrode and tested for electrooxidation of methanol in alkaline media. More specifically, the response for methanol electrooxidation at the NiCu alloy modified electrode is significantly larger than the response obtained for pure electrodeposited Ni.

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Electro-oxidation of saccharose on nickel in alkaline solution

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Electrocatalytic processes involving the oxidation of sugars are of great interest in many areas, ranging from medical applications to wastewater treatment, from the construction of biological fuel cells to analytical applications in the food industry [1–3]. On the other hand, the electrochemical detection of carbohydrates is important in many areas [4].

The electrochemistry of carbohydrates on various electrode materials, e.g. Au, Pt, Ni, Cu and glassy carbon continues to be of interest as these materials could find use for a fuel [5]. The purpose of the present work is to study the electrochemical oxidation of saccharose on a nickel electrode in a solution of 1 M NaOH.

The electro-oxidation of saccharose on nickel in alkaline solutions has been studied by the method of cyclic voltammetry. It has been found that in the course of an anodic potential sweep the electro-oxidation of saccharose follows the formation of Ni (III) and is catalyzed by this species through a mediated electron transfer mechanism.

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Synthesis and application of nanoporous carbon as an electrocatalyst support for electrooxidation of methanol in direct methanol fuel cell

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Carbon materials have been applied in various areas, including gas separation, catalyst support and electrodes for electrochemical devices. Various meso and nanoporous carbon materials with pore size from 2 to 50 nm have been synthesized using nanostructured silica materials as templates [1].

Here we report on the synthesis of nanoporous carbon from polymer-silica composites, which were synthesized by phloroglucinol-formaldehyde [2]. (PF) polymerization in the presence of uniform size silica particles using KOH as the base catalyst. After carbonization and subsequent removal of the silica template, the polymer-silica composites turned into nanoporous carbon with high surface area. The resulting nanoporous carbons were characterized by X-ray powder diffraction, nitrogen adsorption isotherm and thermogravimetry. The surface area of the PF-based nanoporous carbon was ~ 900 $m^2 g^{-1}$.

Platinum was anchored on the nanoporous carbon by the microwave assisted polyol process and the resulting supported catalyst was used as the electrocatalyst for methanol oxidation in acidic solutions. The results indicated that electrooxidation of methanol occurs at a lower potential with higher electrocatalytic activity compared to the same catalyst on the conventional support (Vulcan XC-72R). This can be related to high surface area of the nanoporous carbon which significantly increases the metal disperation and effect particle size, resulting in favoured electrochemical processes during methanol oxidation [3].

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NOVEL NANOSTRUCTURE ANODE FOR DIRECT METHANOL FUEL CELL (DMFC)

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Keyword; Nanostructure, Direct methanol fuel cell, polyaniline Nanofibular, methanol electro-oxidation.

The aim of this work is to present a novel nanostructure anode for DMFC using polyaniline (PANI) modified anode. In this work anode electrode prepared using addition of PANI nanofibers on the surface of anode catalyst layer with electropolymerization of aniline and trifluoromethane sulfonic acid (TFMSA) under Galvanostatic conditions.

The test results (figure A) under steady state conditions indicate MEA made by PANI modified anode exhibits better performance than commercial MEA (from fuel cell store) made by alloyed catalyst and high metal content. Figure B, shows the performance of modified anode in DMFC under different temperatures. As you can find new modified MEA has good stability in different operational conditions.

Finally, the test results of the different fuel flow rate in the anode side promotes PANI can act as barrier for methanol crossover from the anode to the cathode side. This conclusion attributed to increasing of catalyst activity of the polyaniline modified anode for methanol oxidation and improvement of electron and proton conductivity of the polyaniline nanofiber modified anode.

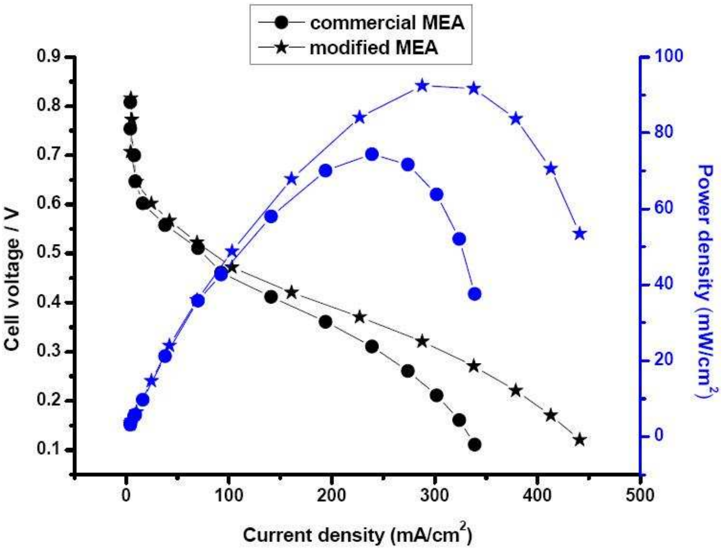

Figure A. The performance of modified and commercial MEAs in DMFC at 80 oC, fuel:1M MeOH fuel flowrate:1 ml/min, Oxidant: O2, O2 flowrate: 0.2 L/min-ambient,

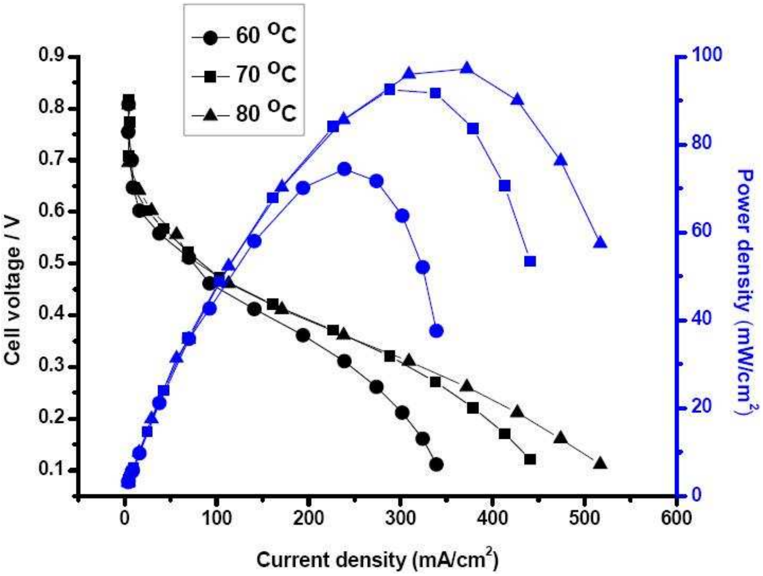

Figure B. The performance of modified MEAs in DMFC at different temperatures, fuel: 1M MeOH fuel flowrate: 1 ml/min, Oxidant: O_2, O_2 flowrate: 0.2 L/min-ambient,

Monitoring of the Anode Dry out at High Current Censity in H2/O_2 and H_2/air PEMFC Stack

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The polymer electrolyte fuel cell (PEFC) is of great interest in energy research because of its high efficiency, high power density, low pollution and low operating temperature [1, 2].

But they have to overcome some engineering and economic problems in order to be a commercial success. In particular, humidification is accompanied by energy loss. Hence, operation under optimal humidified conditions is of great advantage for improved energy conversion efficiency.

However, it is considered that low humidified gas conditions accelerate the decay of the electrolyte membrane, which is a key material for the PEMFC and high humidified gas conditions causes electrodes flooding. The stability of the membrane is determined by its water content. Proper hydration of the membrane is critical for maintaining membrane conductivity and mechanical stability [3, 4]. In fact, the upper limit of the operating temperature of conventional PEMFCs using per-fluorinated ionomers is dictated by the need to maintain the membrane water content. Therefore, the relative humidity of fuel and oxidant gases influences the voltage performance and stability.

Excellent life performance probably requires highly humidified conditions and it is necessary to keep the homogeneous water content in the membrane under even lower humidified conditions. This article is concerned on anode dry out at high current density in H2/O2 and H2/air PEMFC under different operation conditions to get some idea in flow fields designing for stack applications.

Test results indicate that at high current density since a lots of water transfers from the anode to the cathode side, the anode is in a dry condition, while the cathode is in a high humidity condition. The low pressure and flow rate in the cathode induce stagnation of water, which floods the cathode at the oxygen utilization of 80%. Moreover, in case of using the air in the cathode, cell shows a high resistance because of the low oxygen partial pressure. In any event, this failure can be avoided by the redesign of the gas flow channel in fuel cell stack.

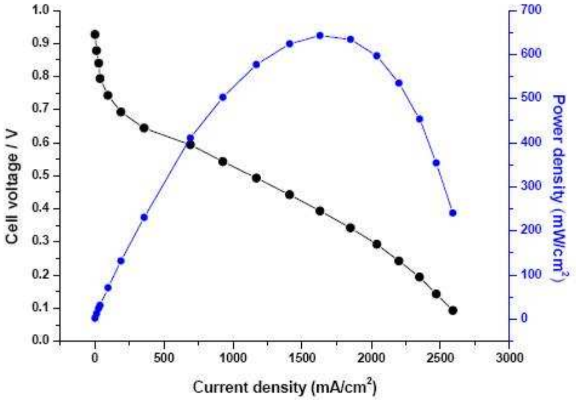

Figure A. The performance of H2/O2 PEMFC in the following condition: T anode /T cell / T cathode: 70 /60/50 °C Anode pressure: ambient Cathode pressure: ambient H_2 and O2Flowrate: 0.1and 0.2 L/min

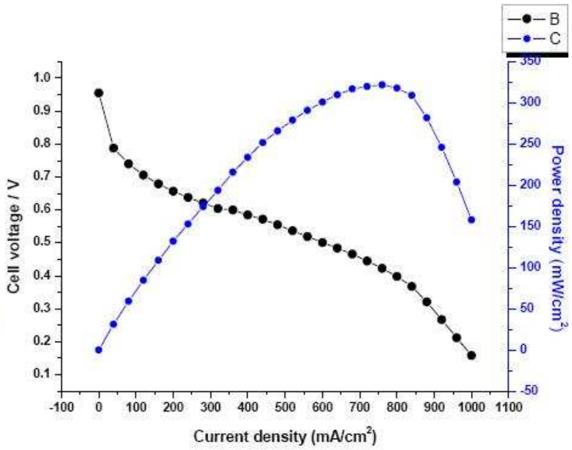

Figure B. The performance of H2/air PEMFC in the following condition: T anode /T cell / T cathode: 70 /60/50 °C Anode pressure: ambient Cathode pressure: ambient H_2 and air Flow rate: 0.1and 0.2 L/min

Hydrogen and fuel cell technologies, related challenges and European proposal roadmap for the 21st century

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1. Abstract

In this report we try to highlight the need for strategic planning and increased effort on research, development and deployment of hydrogen and fuel cell technologies. It also makes wide ranging recommendations for a more structured approach to European energy policy and research, for education and training, and for developing political and public awareness. Foremost amongst the recommendations is the establishment of a European hydrogen and fuel cell technology partnership and advisory council to guide the process.

2. Introduction

Energy is the very lifeblood of today’s society and economy. Our work, leisure and our economic, social and physical welfare all depend on the sufficient, uninterrupted supply of energy. Yet we take it for granted and energy demand continues to grow, year after year. Traditional fossil energy sources such as oil are ultimately limited and the growing gap between increasing demand and shrinking supply will, in the not too distant future, have to be met increasingly from alternative primary energy sources. We must strive to make these more sustainable to avoid the negative impacts of global climate change, the growing risk of supply disruptions, price volatility and air pollution that are associated with today’s energy systems. The energy policy of the European

Commission advocates securing energy supply while at the same time reducing emissions that are associated with climate change. This calls for immediate actions to promote greenhouse gas emissions-free energy sources such as renewable energy

Sources, alternative fuels for transport and to increase energy efficiency. On the technology front, hydrogen, a clean energy carrier that can be produced from any primary energy source, and fuel cells which are very efficient energy conversion devices, are attracting the attention of public and private authorities. Hydrogen and fuel cells, by enabling the so-called hydrogen economy, hold great promise for meeting in a quite unique way, our concerns over security of supply and climate change.

Hydrogen and fuel cells are seen by many as key solutions for the 21st century, enabling clean efficient production of power and heat from a range of primary energy sources. The High Level Group for hydrogen and fuel cells technologies was initiated in october 2002 by the vice president of the European Commission, Loyola de Palacio, Commissioner for energy and transport, and Mr. Philippe Busquin, Commissioner for research. The group was invited to formulate a collective vision on the contribution that hydrogen and fuel cells could make to the realisation of sustainable energy systems in future.

3. Conclusions

Moving Europe away from its 20th century dependency on fossil fuels to an era powered by the complementary energy carriers, electricity and hydrogen will require careful strategic planning.

Hydrogen is not likely to be the only fuel for transport in future. Moreover, maintaining economic prosperity during the transition period will involve maximising the efficient use of various forms of fossil-based energy carriers and fuels such as natural gas, methanol, coal, and synthetic liquid fuels derived from natural gas. During that time it will also be important to introduce renewable energy sources such as biomass, organic material – mainly produced by the agriculture and forestry sectors that can be used to generate heat, electricity, and a range of fuels such as synthetic liquid fuels and hydrogen. Where appropriate, traditional forms of electricity generation can be harnessed to produce hydrogen through the electrolysis of water, while employing new, safe technologies and renewable sources to minimize harmful emissions of greenhouse gasses and pollutants.

Throughout the period, electricity from renewable energy sources can be increasingly used to generate hydrogen.

The ability to store hydrogen more easily than electricity opens up interesting possibilities for storing energy, helping to level the peaks and troughs experienced in the electricity generating industry. Hydrogen fuelling stations can be erected, using locally or industrially produced hydrogen. Given the complex range of options, a framework for the introduction of hydrogen and fuel cells needs to be established. This transition should be executed progressively along the following broad lines:

In the short and medium term (to 2010):

- Intensify the use of renewable energy sources for electricity which can be used to produce hydrogen by electrolysis or fed directly into electricity supply grids
- Improve the efficiency of fossil-based technologies and the quality of fossil-based liquid fuels
- Increase the use of synthetic liquid fuels produced from natural gas and biomass, which can be used in both conventional combustion systems and fuel-cell systems
- Introduce early applications for hydrogen and fuel cells in premium niche markets, stimulating the market, public acceptance and experience through demonstration, and taking advantage of existing hydrogen pipeline systems
- Develop hydrogen-fuelled IC engines for stationary and transport applications, supporting the early deployment of a hydrogen infrastructure, providing they do not increase the overall CO2 burden

In the medium term (to 2020):

- Continue increasing the use of liquid fuels from biomass

- Continue using fossil-based liquid and gaseous fuels in fuel cells directly, and reforming fossil fuels (including coal) to extract hydrogen. This enables transition to a hydrogen economy, capturing and sequestering the CO2.

The hydrogen thus produced can then be used in suitably modified conventional combustion systems, hydrogen turbines and fuel-cell systems, reducing greenhouse gas and pollutant emissions

- Develop and implement systems for hydrogen production from renewable electricity, and biomass. Continue research and development of other carbon-free sources, such as solar thermal and advanced nuclear sources

In the medium to long term (beyond 2020):

- Demand for electricity will continue to grow, and hydrogen will complement it. Use both electricity and hydrogen together as energy carriers to replace the carbon-based energy carriers progressively by the introduction of renewable energy sources and improved nuclear energy. Expand hydrogen distribution networks.

Maintain other environmentally benign options for fuels.

At the end of this report, a challenging European hydrogen & fuel cell vision has been presented.

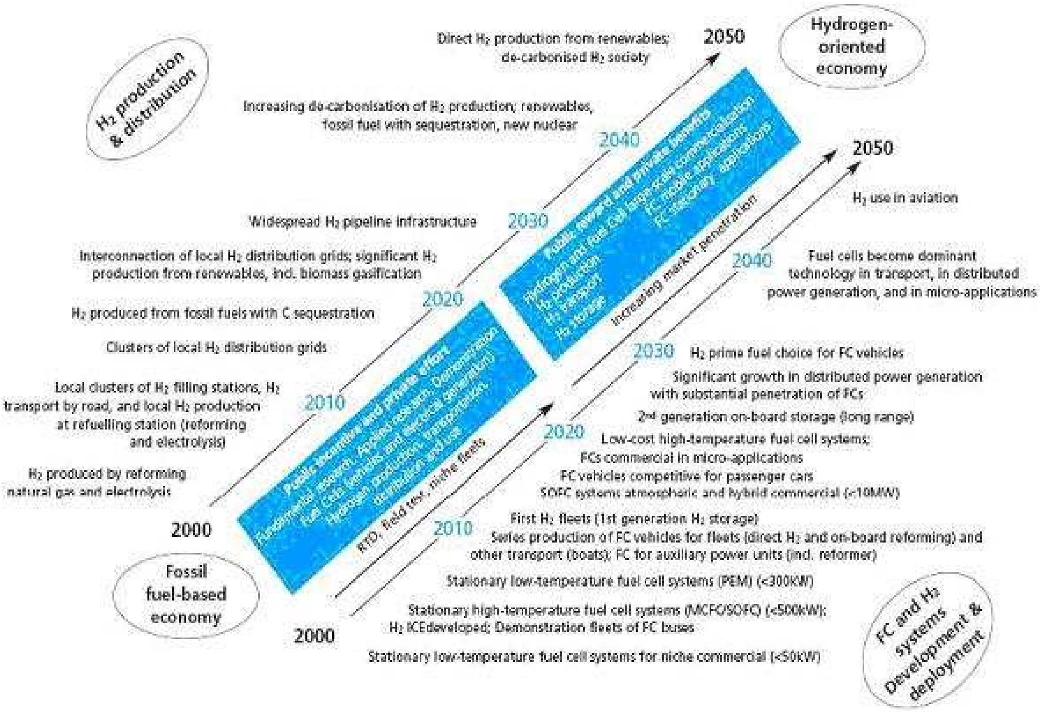

Figure 1: Skeleton proposal for European hydrogen and fuel cell roadmap

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Synthesis of platinum nanoparticles by electroless method for polymer electrolyte membrane fuel cell

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Abstract

An electroless deposition method (i.e., the conventional impregnation method) has been developed to grow highly dispersing Pt nanoparticles for proton exchange membrane fuel cells (PEMFC). Pt nanoparticles with sizes ranging from 5 nm to 25 nm were synthesized on carbon nanotubes. This electrode preparation method has the advantages such as the ease of preparation and a good control for lowering the platinum-loading.

Keywards: electroless method, Electrode, synthesize, nanoparticle, PEMFC

Introduction

Proton exchange membrane fuel cell (PEMFC) has been attracting much attention as future energy sources for potential stationary, portable, or automotive applications[1]. A broad commercialisation of PEMFCs requires, however, an important reduction in the cost of components such as electrocatalysts, ionomer membranes, membrane electrode assemblies (MEAs) and bipolar plates [2].

At present, platinum or platinum alloys are the catalysts of choice for PEM fuel cells due to their high catalytic activity and their stability in the fuel cell environment; these

Electrocatalysts are expensive and thus, there is a need to minimize the catalyst loading and maximize the catalyst utilization, without sacrificing catalytic activity.

As the catalytic reduction of oxygen and the catalytic oxidation of hydrogen are surface processes, a way to maximize catalyst utilization is to maximize the specific surface area of platinum [3].

For Pt catalyst reduction, two approaches are currently very active: exploration of non-noble catalysts, and reduction of Pt loading. The electrocatalytic activity of platinum catalyst is dependent on many factors [4]. Among them, the good properties of the catalyst supports, such as high surface area and good electronic property, are essential for Pt catalyst to produce high catalytic activity. Carbon nanotubes (CNTs), Due to their nanometer size and interesting properties such as high accessible surface area, low resistance and high stability are also of great interest for many applications [5].

The main purposes for using CNTsupported Pt catalysts are to reduce Pt loading through increasing the catalyst utilization, and improving the catalyst activity/performance.

Experimental

Prior to Pt deposition onto the MWNTs, the MWNTs were surface oxidized by refluxing in a HNO3 for 12 h at 120°C. The solid phase was removed by centrifugation and washed with distilled water; the recovered MWNTs were dried at 80°C for 12 h. Then CNTs with H2PtCl6 was refluxed with diluted ethylene glycol for 6 h at 110 °C. Following reflux, the mixture was allowed to cool to room temperature and then centrifuged for 30 min at 6000 rpm. The wet solids were washed many times with deionized water, filtered and dried at 80 °C for 4 h.

Results obtained by TEM analysis of these samples,reported in Fig. 1, show the spherical shape of Pt well dispersed on the carbon nano-tube surface with uniform size distribution centered at 5-25nm. (The small dark particles assigned to Pt particles were well dispersed on the CNT surfaces).

Fig 1. TEM images of Pt/MWNT

Conclusions

The electroless deposition method was used to prepare platinum nanoparticles on MWNT. By using this method Pt nanoparticles, about 5-25 nm in diameter, were dispersed uniformly on the carbon nanotube. The advantages of this method are simplicity and suitable dispersion of nanoparticles in the reaction media. The disadvantages of this process are lack of the control of the nanoparticle size and the longer time of reaction. By suitable dispersion of these nanoparticles, the generation of the active sites and increase of the surface area of nanoparticles, the larger current densities were gained and will be studied in the further experiments.

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Preparation of Pt/C catalyst using reverse micelle method for oxygen reduction reaction in PEM fuel cells

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Abstract

Synthesis of carbon-supported Pt/C catalysts using a new preparation technique, a reverse micelle method, is reported. Platinum nanocatalysts supported on Vulcan XC-72 carbon have been synthesized through the reduction of chloroplatinic acid with Sodium borohydride, using reverse micelles as nanoreactors in the cyclohexane medium. The performance of the Pt/C catalysts was tested by three-compartment electrochemical cell technique.

Keywords: PEM fuel cell, Reverse micelle, Surfactant, Pt/C catalyst

Introduction

One of the obstacles preventing polymer electrolyte fuel cells from commercialization is the high cost of noble metals to be used as catalyst, such as platinum and ruthenium. Another is low performance of the oxygen reduction reaction at the cathode. Although expensive platinum-based catalysts seem to be the best catalyst for the oxygen reduction reaction at the cathode so far, they are still at least 10^6 times less active for oxygen reduction than for H_2 oxidation at the anode. To effectively use platinum, improve catalytic performance of oxygen reduction and decrease the amount of platinum, it has to be well dispersed to small particles on conductive carbon supports. Nanoparticles are unique materials and have a broad application in the homogeneous and in the heterogeneous catalysis [1]. The uniqueness of these nanoparticles is mainly because of their large surface area and specific functions which are different from those of either bulk metal particles. It is well-known that the higher surface area, which relates to the increase of reacting sites, could be achieved when the size of particles decreases [2]. Conventional methods, such as impregnation, co-precipitation and ion exchange, are not adequate from the viewpoint of offering high metal surface area or good dispersion of metal particles [3]. To avoid the above disadvantages, one of the most effective preparation method of nanoparticles is water-in-oil microemulsion media or a reverse micelle (RM) method [4-6]. In a reverse micelle, the polar groups of the surfactants are concentrated in the interior and the lipophilic groups extend toward and into the nonpolar solvent. Reverse micelles consist of nanometer-sized water droplets that are dispersed in an oil medium and stabilized by surfactants. These reverse micelle systems are heterogeneous on a molecular scale; nevertheless, they are thermodynamically stable. Reverse micelle systems are suitable reaction media for the synthesis of nanoparticles because tiny droplets of water are encapsulated into reverse micelles. Water pools of these reverse micelles act as microreactors for performing simple reactions of synthesis, and the size of microcrystals of the product is determined by the size of these pools. The size of the water pools is known to be controlled by the molar water/surfactant ratio in the system. A cosurfactant is used to help decrease the fraction of the micelle head group that is neutralized and thereby increase the stability of the micelle. The reverse micelle method is used to make perfect particle control over particle size and uniformity be practicable. On the other hand, it does not require extremely high temperature and pressure conditions or any special equipment. The reverse micelle method is widely used in production of metallic nanoparticles, semiconductor materials, and nanometer-scale magnetic particles [7-11]. In this study, we prepared Pt nanoparticles using a reverse micelle method, and then deposited those nanoparticles on carbon (XC-72) to obtain Pt/C catalysts.

Experimental

Materials

Hexachloroplatinic acid, surfactant cetyl triethyl ammonium bromide (C16TAB) and Nafion 5% solution were purchased from Aldrich. Sodium borohydride, sulfuric acid, cyclohexane and 1-butanol were obtained from Merck. Vulcan XC-72 carbon was procured from E-TEK.

Synthesis of Pt nanoparticles

Reverse micelle solutions consisted of an oil phase cyclohexane, surfactant, and cosurfactant 1-butanol. An aqueous phase containing the reactant H_2PtCl_6 was used to form the reverse micelle. Another aqueous phase containing the reducing agent $NaBH_4$ was also used to form another reverse micelle. A 0.5 g portion of C16TAB, 6.5 mL of 1-butanol, 20 mL of cyclohexane and 5 mL of 3 mM H_2PtCl_6 solution were added in a 250 mL, three-neck flask reactor under Ar atmospheric conditions, and the mixture was stirred at room temperature for 30 min to form the reverse micelle (I). A 0.5 g portion of C16TAB, 6.5 mL of 1-butanol, 20 mL of cyclohexane, and 6 mL of 40 mM $NaBH_4$ were added in a flask under Ar atmospheric conditions to form a reverse micelle (II). The reverse micelle (II) was then transferred into the reverse micelle (I). Pt nanoparticles were formed when H_2PtCl_6 solution and reducing solution $NaBH_4$ contacted each other. The color of the solution changed to dark from orange due to the suspended reduced metal nanoparticles. The reaction was allowed to mix for 2 h under Ar.

Preparation of Carbon-Supported Pt Catalysts

The appropriate amount of carbon (XC-72), dispersed in cyclohexane under ultrasonic wave agitation for 30 min, was added to the above micelle solution containing Pt nanoparticles under constant stirring over 8 h (or overnight). A 50 mL portion of ethanol was then added to this mixture to break this reverse micelle, and the mixture was allowed to continue to stir 30 min; the supported carbon precipitated. The precipitate was centrifuged using a centrifuge with 8000 rpm. After washing with 1:1 water and ethanol, cyclohexane and acetone, the product was dried at 120- 140 °C under vacuum over 8 h (or overnight).

Preparation of Working Electrode

Carbon paper served as an underlying substrate of the working electrode. The catalyst ink was prepared by ultrasonically dispersing 5.2 mg of 10 wt % of Pt/C in 4 mL of isopropyl alcohol-H_2O, to which 0.3 mL of 5 wt % of Nafion solution was added and the dispersion was then ultrsonicated for 30 min. A quantity of 1.3 mg of the dispersion was pipetted out on the carbon paper that have gas diffusion layer.

Electrochemical measurement

The catalysts were electrochemically characterized by cyclic voltammetry (CV), linear sweep voltametry (LSV), chronoamperometry and impedance spectroscopy using an electrochemical work station. Electrochemical experiments were carried out on EG&G Park potentiostat/galvanostat Model 273A (Princeton Applied research). A conventional three-compartment electrochemical cell was used with an Ag/AgCl (saturated KCl) electrode as the reference, a platinum plate (1 cm^2 area) as the counter electrode, and a carbon paper electrode covered with a layer of catalysts as the working electrode. All potentials were measured and reported versus the Ag/AgCl (saturated KCl) electrode.

Results and discussion

Figure 1 show cyclic voltammograms for H adsorption on Pt/C (synthetic and E-TEK). Characteristic peaks in the negative region (0-0.1 V) are attributed to atomic hydrogen adsorption on the Pt surface and reflect the ECSA of Pt.

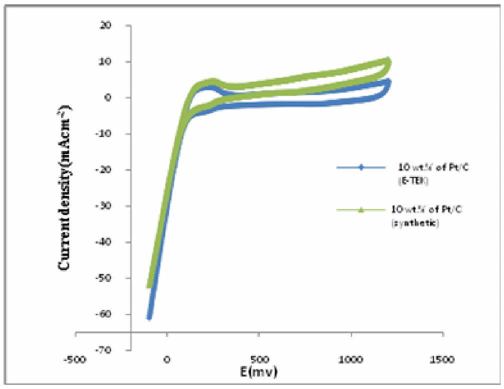

Fig. 1. Cyclic voltammogram of synthetic and E-TEK Pt/C catalysts in 2 M H_2SO_4. Scan rate = 50 mVs^{-1}

Figure 2 show linear sweep voltamograms of two Pt/C catalyst. Curves show that the synthetic catalyst has greater tafel slope than the purchased Pt/C and thus has less polarization.

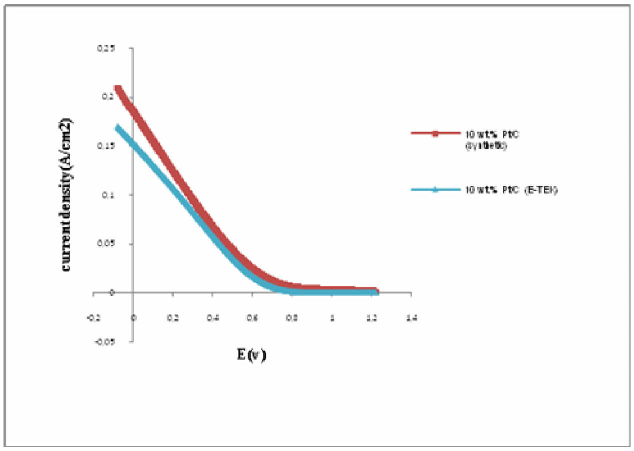

Fig. 2. Linear sweep voltammograms of Pt/C catalysts (synthetic and E-TEK) in 2 M H_2SO_4 solution at 25˚C. Sweep rate = 1 mVs^{-1}

The impedance plots in Figure 3 show that similar high frequency resistance was obtained for both the E-TEK and synthetic catalysts . This indicates that the surfactant will not introduce additional resistance to the MEA.

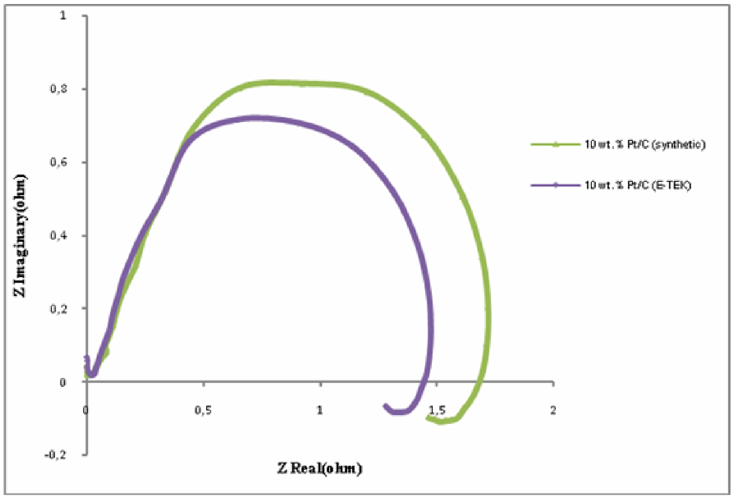

Fig. 3. Experimental impedance plots for 10 wt.% synthetic Pt/C and E-TEK 10 wt.% Pt/C.

Conclusion

We have reported synthesis of Pt nanoparticles by reducing H_2PtCl_6 in a reverse micelle system and preparation of Pt/C catalysts by depositing the Pt nanoparticles on carbon (on Vulcan XC-72). Catalytic activities for the oxygen reduction reaction on Pt/C catalyst were evaluated by A conventional three-compartment electrochemical cell with an Ag/AgCl (saturated KCl) electrode as the reference, a platinum plate (1 cm^2 area) as the counter electrode, and a carbon paper electrode covered with a layer of catalysts as the working electrode. The results indicated that the synthesized Pt/C catalysts possess better catalytic activity for the oxygen reduction reaction than purchased E-TEK Pt/C catalyst. All the above-mentioned results implied that many factors influenced the catalytic activity of the oxygen reduction reaction, such as preparation method, type of surfactant and catalyst preparation conditions.

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Preparation of Pt/C as a catalyst for PEMFC Stabilized by Ethylenediaminetetraacetic Acid Disodium Salt

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Abstract

A novel method with ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) as a stabilizing agent was developed to prepare highly dispersed Pt nanoparticles on carbon (vulcan xc-72) to use as proton exchange membrane (PEM) fuel cell catalysts. These nanocatalysts were obtained when the EDTA-2Na/Pt ratio was maintained at 1:1. And the Pt/CNT catalyst exhibited large electrochemical active surface areas, very high electrocatalytic activity. The Pt/XC-72R catalyst with narrow size distribution was prepared by this method.

Keywords: Ethylenediaminetetraacetic acid disodium salt stabilizer, Proton exchange membrane fuel cells (PEMFC), Pt/C catalyst

Introduction

Proton exchange membrane (PEM) fuel cells have become a favorable future power source because of their low operating temperature, high power density and environmentally friendly technology [1,2,3]. Electrocatalysts with high activity at room temperature are critically needed to enhance their performance for commercial device applications. Supported Pt and Pt alloys catalysts are the most promising catalytic materials for fuel cells to meet the key requirements for their high electrocatalytic activity [1,4,5]. It is well known that the special activity of the metal supported catalysts is strongly dependent on the particle size, size distribution and support [1]. Nevertheless, The common criteria for a high performance catalyst are: (1) a narrow nanoscale size distribution; (2) a uniform composition throughout the nanoparticles; (3) a fully alloyed degree; (4) high dispersion on carbon support. According to these criteria, some innovative and cost-effective preparation methods have been developed and show promise for reaching performance optimization by controlling synthetic procedures and conditions. Carbon blacks are commonly used as supports for DMFC anode catalysts. There are many types of carbon blacks, such as Acetylene Black, Vulcan XC-72, Ketjen Black, etc. These carbon blacks show different physical and chemical properties, such as specific surface area, porosity, electrical conductivity and surface functionality. Among these factors, specific surface area has a significant effect on the preparation and performance of supported catalysts.Vulcan XC-72 with a surface area of □250m2 g−1 has been widely used as a catalyst support [6]. Some alternative synthesis methods for the Carbon-supported metal particles are metal vapor deposition and chemical reduction deposition in the solution phase [1,7]. These approaches were often considered to lack good control of particle size, shape and distribution [1]. Recently, an increasing interest has been shown to use some kind of stabilizing agents, such as surfactants, ligands or polymers, to produce desired sizes of Pt nanoparticles with uniform dispersion on the carbon support. Prabhuram et al. [8] developed a process to synthesize Pt/C nanocatalysts using surfactant tetraoctylammonium bromide (TOAB) as the stabilizer. Chen et al. [9] reported a technique using a polymer, poly-(vinylpyrrolidone) (PVP), in a polyol solution to mediate the size of Pt nanoparticles and control their size distribution. Mu et al. [10] prepared well-dispersed Pt nanoparticles on CNTs by modifying Pt with organic molecule triphenylphosphine (PPh3). Liao et al. [4] have synthesized CNT-supporting ternary PtRuIr catalysts having very small particle sizes and excellent activity for the oxidation of methanol by using citrate as a complexing agent. However, close examination of these methods reveals that they involved a tedious treatment procedure to remove the organic layer so as to achieve metal particles on the nanoscale with greater uniformity. Hence, it is desirable to develop a simple and effective synthesis route that provides well-dispersed Pt nanoparticles while maintaining some degree of control of particle size.

In the present investigation, we report the synthesis of 20wt% Pt nanoparticles on the Vulcan XC-72 , with ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) as a stabilizer and formaldehyde as a reducing agent in the acetone/H2O solution. EDTA is the most commonly used chelator for heavy metal detox. EDTA attaches itself to heavy metals and carries the metals from the body. EDTA can also slow free-radical activity produced by heavy metals in the body. The EDTA-2Na is carefully chosen because it has four carboxyl anions and two nitrogen-containing groups, which can adsorb on the surface of metal particles and exert either steric hindrance or coulombic effects on the metal particles, thereby stabilizing them. In addition, it can be easily removed from the particle surface by water washing or extraction.

Experimental

Materials

All the chemicals used were of analytical grade. H2PtCl6 .6H2O and ethylenediaminetetraacetic acid disodium salt were purchased from Merck Company. Methanol, acetone, ethanol, sulfuric acid, formaldehyde, 65% HNO3, 30% H2O2 and NaOH (all from Merck Company) were used as received. Nafion (5wt% solution) was obtained from Aldrich Company.Carbon papers were purchased from E-TEK.

Catalyst Preparation

Firstly, carbons were put into acetone and shaked for 30 min at room temperature, then filtered and heated to get dry powder. Secondly, the powder was added to the mixture of 10%HNO3 and 30%H2O2 at 70 °C, and the solution was refluxed for 3 h, then filtered, washed with distilled water, heated and milled. The detailed catalyst preparation process can be described as follows: (i) 100 mg of pretreated carbon vulcan were added to a mixture of acetone/H2O (2:1/v:v) solution (15 ml), and ultrasonicated for 30 min. (ii) For synthesizing the Pt/C with EDTA-2Na/Pt ratio of 1:1, the corresponding 0.0576 g of EDTA-2Na in 5 ml of water was added to 10 ml of 1.544 × 10–2 M H2PtCl6 · 6H2O in water. Then the PH value of the mixture was adjusted to 7–8 by aqueous NaOH solution (0.1 M) under vigorous stirring. (iii) The obtained yellow solution was mixed with the carbon/acetone/H2O solution homogeneously, and formaldehyde/water solution (4 ml, 37%) was added drop by drop. The resulting mixture was stirred at 60°C for 7 h until colorless. During the reaction process, the pH value of the system must be maintained within 7–8 by addition of a NaOH aqueous solution (0.1 M). Finally, the products were filtered, washed with excess deionized water, and then dried at 90 °C.

Electrochemical Measurement

The catalyst were electrochemically characterized by cyclic voltammetry (CV), linear sweep voltammetry(LSV) and impedance spectroscopy using a potentiostat and galvanostat (EG&G Princeton, Model 273A and FRD model 1025). A conventional, three-electrode system consisting of carbon paper in holder with an area 1 cm2 as the working electrode, and Pt plate as the counter electrode and Ag/AgCl as the reference electrode was used. The Pt loading on electrode was 0.2 mg/cm2. The electrochemical experiments were performed in 2 M H2SO4 solution.

Results and Discussion

Figures 1-3 show the electrochemical experiments of Pt/C nanocatalysts prepared with this technique that molar ratio of EDTA-2Na/Pt was 1:1.

The cyclic voltammogrames and linear sweep voltammogrames show that synthesized Pt/C 20% has more ECSA and activity than purchased Pt/C 10%.

In the impedance spectroscopy, Frequency range was 100kHz -10 mHz , AC amplitude was 5 mV rms and data quality was 1.below figure shows the impedance spectroscopy of two kinds of Pt/C.

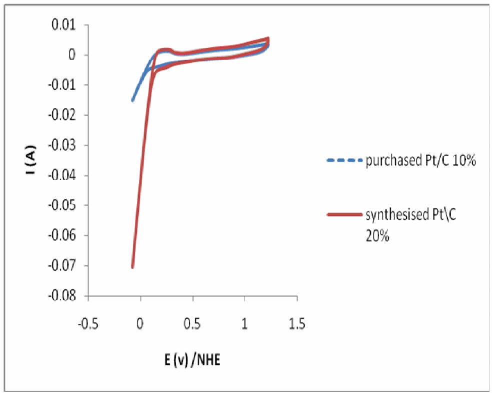

Figure 1. cyclic voltammogram of synthesised Pt/C(20 wt%) and purchased Pt/C 10% in 2M H_2SO_4 ,Pt loading in carbon paper was 0.2 mg/cm^2.scan rate was 50 mv/s

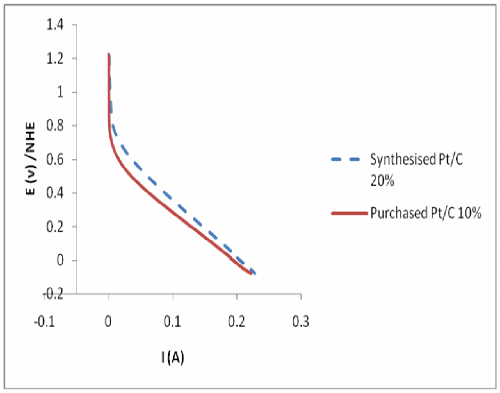

Figure 2. linear sweep voltammogram of synthesised Pt/C(20 wt%) and purchased Pt/C 10% in 2M H_2SO_4 ,Pt loading in carbon paper was 0.2 mg/cm^2.scan rate was 1 mv/s

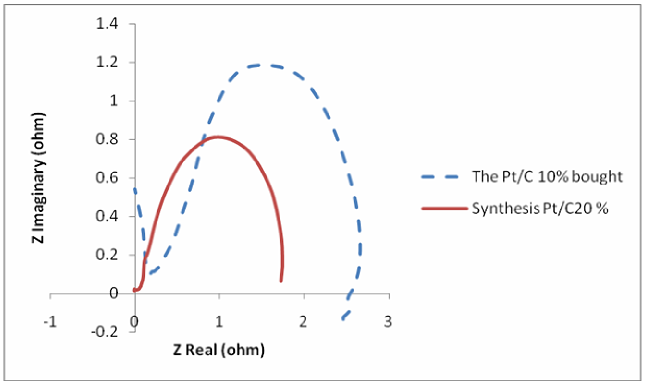

Figure 3. impedance spectroscopy of synthesis Pt/C(20 wt%) and the purchased Pt/C 10% in 2M H_2SO_4 ,Pt loading in carbon paper was 0.2 mg/cm^2

The impedance spectroscopy shows that synthesis Pt/C has less resistance than the Pt/C 10% was bought.

Conclusions

A simple, fast and energy efficient method has been successfully developed for the preparation of Pt/XC-72R catalysts with high electrocatalytic activity. It is unique in the system that the EDTA-2Na exhibits excellent stabilization effect and sufficient protection for Pt nanoparticles from being aggregated. The very high activities and low resistance of Pt/C catalyst could attest to the excellent dispersion of the metal nanoparticles. The present technique can be used as a general method to prepare other supported metal particles from metal precursors.

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Effect of synthesis pH on the electrocatalytic activity of Ru_xSe_y prepared by the microwave polyol process for oxygen reduction reaction (ORR)

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The electrocatalytic conversion for the direct four electron reduction of oxygen to water is extremely important in the clean energy industry. In fuel cells, Pt supported on carbon is usually used as the catalyst for the electroreduction of oxygen. Depolarization of the Pt cathode in direct methanol fuel cells, due to methanol crossover, results in considerable voltage losses [1]. Ru_xSe_y nanoparticles have a reasonable high catalytic activity and methanol-tolerance for ORR [2]. In this paper uniform Ru_xSe_y chalcogenide electrocatalyst supported on carbon (Vulcan, XC-72R) was prepared by the microwave assisted polyol process, in which an ethylene glycol solution of ruthenium (III) chloride and sodium selenite are heated under microwave [3]. It was found that the Ru_xSe_y characteristics including reaction yield, particle size and electrochemical activity for ORR are highly dependent on pH of the synthesis medium. Rotating disk electrode (RDE) voltammetry was carried out to evaluate the electrocatalytic activity of the Ru_xSe_y chalcogenide catalyst.

Experimental results indicated that the precursors of the reaction including $RuCl_3$ and Na_2SeO_3 are completely reduced at pH 8.0 and the kinetically controlled current density (J_k) at 0.75 (V) versus NHE is highest at this condition. The mean particle size of the catalyst was 2.16 nm. The Ru_xSe_y catalyst was characterized by X-ray diffraction (XRD). The XRD for Ru_xSe_y/C clearly exhibited the characteristic diffraction pattern of metallic ruthenium. The ORR activity of the Ru_xSe_y/C catalyst was compared with the commercial Pt/C catalyst in the presence and absence of methanol. In the absence of methanol, the Ru_xSe_y/C catalytic activity for ORR was comparable with that of Pt/C catalyst. However in the presence of methanol, the Ru_xSe_y/C catalyst exhibited a superior ORR activity than the Pt/C catalyst.

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Improvement of DMFC electrodes by carbon nanotubes

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Introduction

Fuel cells, the energy converting devices with a high efficiency and low (zero) emission, have been attracting more and more attention in recent decades due to high- energy demands, fossil fuel depletions, and environmental pollution throughout the world. For hydrogen gas fed fuel cells at their current technological stage, hydrogen production, storage, and transportation are the major challenges in addition to cost, reliability and durability issues. Direct methanol fuel cells (DMFCs), using liquid and renewable methanol fuel, have been considered to be favorable option in terms of fuel usage and feed strategies. Compared to hydrogen – fed fuel cells, which have a reforming unit, or low capacity in the hydrogen storage tank, the DMFC uses a liquid methanol fuel, which is easily stored and transported and simplifies the fuel cell system [1].

It has been recognized that the success of fuel cell technology depends largely on two key materials: the membrane and the electro catalyst. These two key materials are also directly linked to the major challenges faced in DMFCs, including (1) methanol crossover which can only be overcome by developing new membrane; (2) slow anode kinetics which can only be overcome by developing new anode catalysts. With regards to new DMFC anode catalysts, there are two major challenges, namely, the performance, including activity, reliability and durability, and cost reduction.

To improve the electro-oxidation activities of methanol. Among catalysts, the Pt-Ru alloy has been found to be the most active binary catalyst and is the state-of-the-art anode catalyst for DMFCs. The enhanced activity of the Pt-Ru catalyst when compared with Pt for methanol oxidation has been attributed to both a bi-functional mechanism and a ligand (electronic) effect. The bi-functional mechanism involves the adsorption of oxygen containing species on Ru atoms at lower potentials thereby promoting the oxidation of CO to CO_2.

Experimental

MWNTs used were produced from high-purity graphite in a classical arc-discharge evaporation method. The MWNTs mostly ranging from 4 to 60 nm in diameter are hollow tubular structures with a highly graphite multilayer wall.

10 mg of surface-oxidized MWNTs was suspended in 5 mL of ethylene glycol solution and stirred with ultra sonic treatment for 2 min; 1 mL of hexachloroplatinic acid EG solution (0.01 mg /mL EG) and 1ml of $Rucl_3$ (0.0054mg/mL EG) were added to the solution dropwise also under mechanically stirred conditions for 4 h. NaOH (2.5 M in EG solution) was added to adjust the pH of solution to above 13, and then the solution was heated at 140°C for 3 h to ensure that Pt was completely reduced; the entire EG solution has DI water content of 5 vol%. Refluxing conditions were used to keep water in the synthesis system. The whole preparation process was also conducted under flowing argon. The solid was filtered and washed with 1.5 L of DI water and then dried at 80°C for 8 h.

Results

Fig. 1. Presents CV measurements for the Pt-Ru/CNTs in 1M methanol solution and 1M sodium hydroxide at a scan rate of $10 mVs^{-1}$. The CV feature shows two anodic peaks during scans. An anodic peak during the forward sweep at about 0.55V is corresponding to the methanol oxidation activity and another anodic peak

during the reverse sweep at about 0.45V is due to the removal of incompletely oxidized carbonaceous species formed in the forward sweep [2].

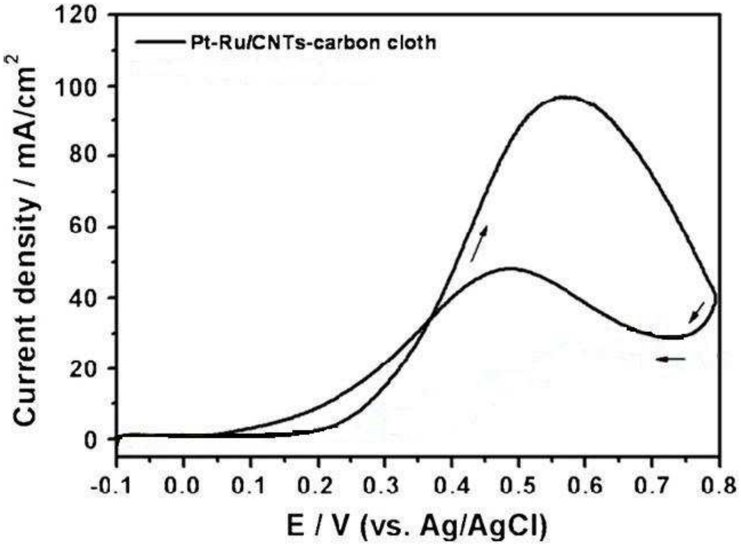

Fig. 1. CV measurements for Pt-Ru on CNTs electrode 1M methanol/1M sodium hydroxide solution at a scan rate of 10mVs−1.

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Kinetic Study of oxygen reduction reaction on platinum particles dispersed in polyaniline film

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Abstract

Oxygen reduction reaction is thermodynamically favored but kinetically slow. Oxygen is used in fuel cell systems as oxidant and fuel cell system is suitable choice for production of clean energy in the present century. For production of more electricity in these systems, the oxygen reduction reaction must be catalyzed. In order to increase reaction rate, polyaniline was used as a substrate for platinum electrocatalyst. After reaching the optimized conditions, the kinetically parameters for oxygen reduction reaction were studied through the rotating disk electrode voltammetry technique and Tafel plot. At the optimized conditions, the results of Koutecky–Levich analysis indicate that the total number of exchanged electrons, symmetry factor and the electron transfer rate constant, are $2.1\bar{e}$,0.412,and $10^{-5.99}cms^{-1}$ respectively. Also, the results of Tafel plot analysis show that the exchange current density and the number of the rate-determining step electrons are $10^{-5.13}Acm^{-2}$ and $1.03 \cong 1\bar{e}$ respectively.

Key words:

Oxygen reduction reaction; Polyaniline; fuel cell; Modified glassy carbon electrode; Platinum; Electrocatalyst.

Introduction

The electrochemical reduction of oxygen is a reaction of considerable interest at the present time, especially in relation to the development of new electrode materials for energy conversion in fuel cells [1]. Therefore, numerous studies [2-8] have been carried out on cathode composition and structure to optimize the utilization of the catalyst and cathode performances.

In this paper, the platinum particles were dispersed in a polyaniline film growth on a glassy carbon electrode to investigate the effect of polyaniline substrate on kinetic of ORR. For the study of the rate of the oxygen reduction reaction, the kinetic parameters were evaluated by the rotating disk electrode voltammetry technique.

Experimental

Platinum modified polyaniline electrodes were prepared in two steps electropolymerization of aniline and electrodeposition of platinum. The electropolymerization of 0.1 M freshly distilled aniline, dissolved in 0.5 M HCL, was carried out, using the cyclic voltammetric technique which sweeps between -200 and 800 mV vs. a saturated calomel reference electrode (SCE), at a sweep rate of 50 mV s^{-1}. This process continued until a film with a thickness of 0.63 μm as determined by the quantity of electricity involved in the redox process of polyaniline, was formed. The counter electrode was a platinum bare electrode. The electrodeposition of various amounts of platinum (0.1- 1 mg cm^{-2}) was carried out at a constant electrode potential, i.e. -200 mV vs. SCE, in a 0.5 M H_2SO_4 solution containing 5×10^{-3} M H_2PtCl_6, 6 H_2O (Merck). Cyclic voltammetric and chronoamperometric experiments were carried out at the room temperature with an Autolab potentiostat/galvanostat PGSTAT20 and the experiments were controlled with general purpose electrochemical system (GPES) software.

Results and Discussion

The reduction of saturated dissolved oxygen at in 0.5 M H_2SO_4 supporting electrolyte was investigated in the GC/PAN/Pt rotating disk electrode for several rotation speeds Ω (from 100 to 400 round per minute). The current vs. potential curves were recorded during a slow voltammetric sweep (sweep rate of 5 mVs^{-1}) between 0.8 and 0.1 V vs. SCE. The current vs. potential curves are shown in Fig. 1.

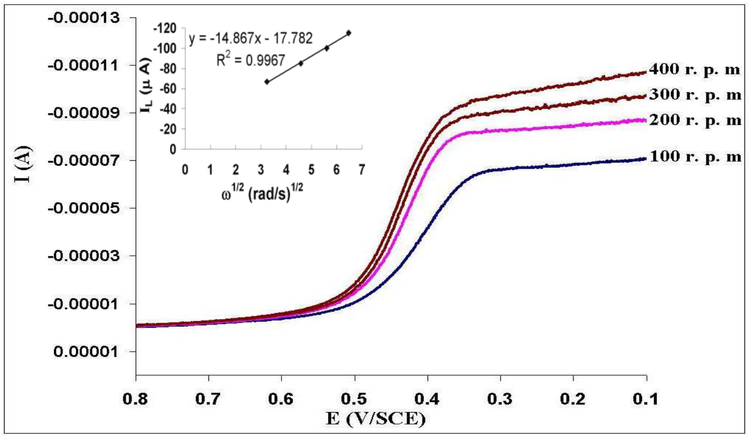

Fig.1. The RDE voltammograms for oxygen reduction in oxygen saturated 0.5 M H_2SO_4 on the modified electrode for various rotation speeds Ω (from 100 to 400 round per minute)(scan rate: 5 mVs^{-1}, platinum loading: 0.8 $mgcm^{-2}$, thickness of polyaniline film: equivalent with 20 scan) The inset shows the variations of oxygen reduction limiting current versus $\omega^{1/2}$

Calculating the slope of curve (the inset of Fig.1.), n was obtained to be $2.1\bar{e}$ at 25°C. For the calculation of the symmetry factor, Koutecky–Levich plots were studied for different electrode potentials. symmetry factor (α) and electron transfer rate constant ($k_\circ$) were calculated to be 0.412 and $10^{-5.99}cms^{-1}$ respectively at 25°C.

Fig. 2 shows Tafel plot for oxygen reduction in O_2-saturated 0.5 M H_2SO_4 on a GC/ PAN/ Pt electrode obtained by voltammogram at a scan rate of 1 mVs^{-1}.

Using the slope of Tafel plot (Fig. 2) and $\alpha = 0.412$ (calculated by rotating disk electrode voltammetry technique), n_α was calculated to be $1.03 \cong 1\bar{e}$ at 25°C. Using the intercept of Tafel plot (Fig.2) $i_\circ$ was obtained to be $10^{-5.13}Acm^{-2}$.

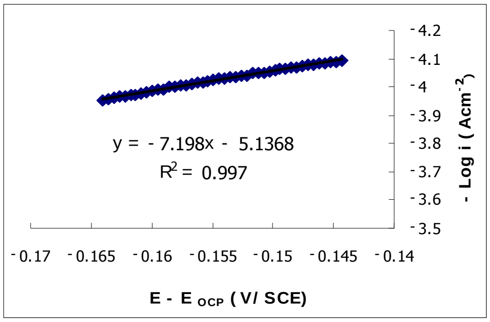

Fig.2. Tafel plot for oxygen reduction in oxygen saturated 0.5 M H_2SO_4 on a GC/ PAN/ Pt electrode at a scan rate of 1 mVs^{-1} (Platinum loading: 0.8 $mgcm^{-2}$, thickness of polyaniline film: 0.63 μm)

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A new dynamic model considering effects of temperature, pressure and internal resistance for PEM fuel cell power modules

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Fuel cell (FC) power planets are electrochemical devices that convert the chemical energy of a reaction directly into the electrical energy .among of a various next-generation power planets ,FCs, especially the proton exchange membrane fuel cells(PEMFCs),are considered to be one of the promising energy sources due to high efficiency and are environment friendly[1]. There are several different types of fuel cells depending on the type of electrolyte materials used. Each fuel cells type has its own characteristics .to design control systems for fuel cells and to compensate its dynamic interactions with rest of the system ,it is necessary to have a reasonably accurate dynamic model .in fact ,there are several fuel cells models reported in the literature; generally speaking, the models can be categorized into two types ,theoretical models based on physical conservation laws and semi-empirical models based on experiments[2-4].

This paper introduces a semi-imperial dynamic model for PEM fuel cell power modules with potential applications in distributed generation. The proposed model is constructed based on the measurement from a NEXTA PEM fuel cell power module under different load conditions and the model has been validated by static as well as dynamic tests. The effects of temperature, pressure of fuel and variations in the internal resistance under different load conditions have been studied. Simulation results have been obtained using the MATLAB and SIMULINK software packages based on the proposed model provides an accurate representation of the dynamic and static behaviors of the fuel cell power modal. the models could be used in PEM fuel-cell control related studies.

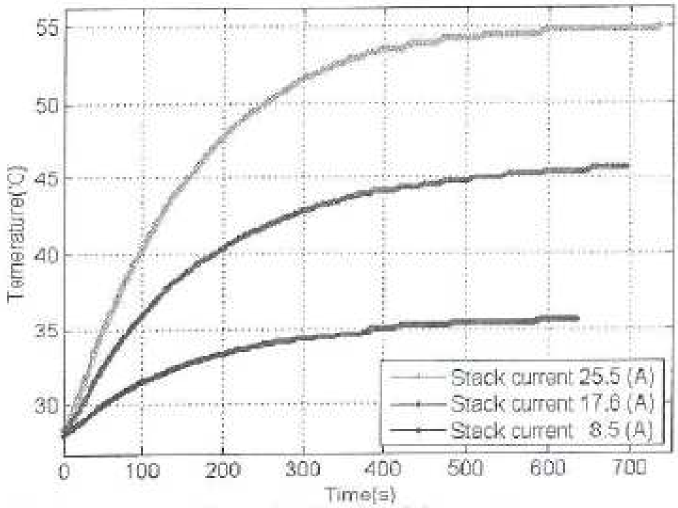

Fig.1. Temperature profile as a function of module current

During experiments, this paper convincingly shows that both the stack temperature and the equivalent internal resistance of the NEXT PEM power module have significant effects on the dynamic characteristics of the fuel cell output. As a result, they should not be ignored. A semi-empirical dynamic model for a NEXT PEM power module considering the characteristics of the temperature and the equivalent internal resistance has been validated using the experimental data. The results have persuasively shown that the developed model can accurately represent the NEXT PEM power module in a wide range of load conditions. Consequently, this model is more suitable for applications in which the load is not a constant.

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Dynamic modeling of a hybrid energy source combined of PEM fuel cell and ultracapacitor

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Fuel cell power plants are electrochemical devices that convert the chemical energy of a reaction directly into the electrical energy. Among the various next-generation power plants, FCs, especially the proton exchange membrane fuel cells (PEMFCs), are considered to be one of the promising energy sources due to high efficiency and are environment friendly [١]. However, for stationary and vehicular applications, a FC power plant may not be sufficient to satisfy the load demands, especially during peak demand periods or transient events. By operating the FC and in parallel, both steady state and peak power demands can be satisfied. Without the ultracapacitor (UC) bank, the FC power plant would have to supply all power demand, thus increasing the size and cost of the FC power plant. The UC bank is used to provide the difference between the load demand and the output power generated by the FC power plant[2,3].

It is recommended to combine fuel cell with other electrical energy storage devices to satisfy sustained load demand and transient events. While batteries have low power density and limited lifetime in highly cyclic application, ultracapacitors can be used. An ultracapacitor (UC) bank can supply a large burst of power but cannot store much energy. By operating the FC and UC in parallel, both steady state and peak power demands can be satisfied. In this paper an improved dynamic model of Nexa^{Tm} PEM fuel cell power module is developed; in addition, it is used to design a hybrid energy source consisting of FC and UC for residential applications. The proposed dynamic model is presented in Matlab/Simulink and SimPowerSystems environment.

To investigate the change in temperatures for different load conditions, the hydrogen pressure is kept at 5 psig. The load connected to the power module is adjusted by varying load resistances. The results of these tests are shown in Fig. 1. as the current changes the temperature of the fuel cell stack also changes, and the rate of the change is proportional to the level of the load.

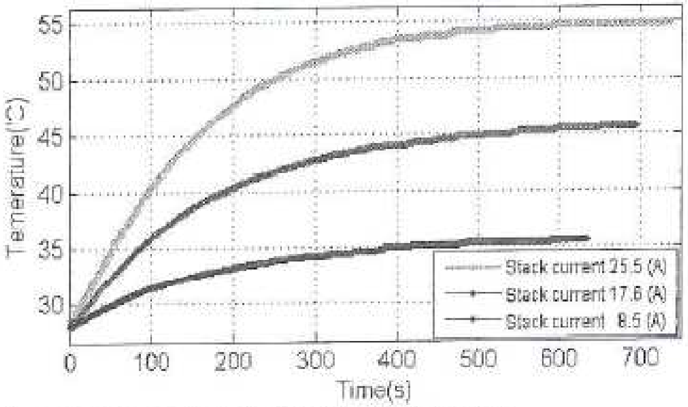

Fig. 1. Temperature profile as a function of module current.

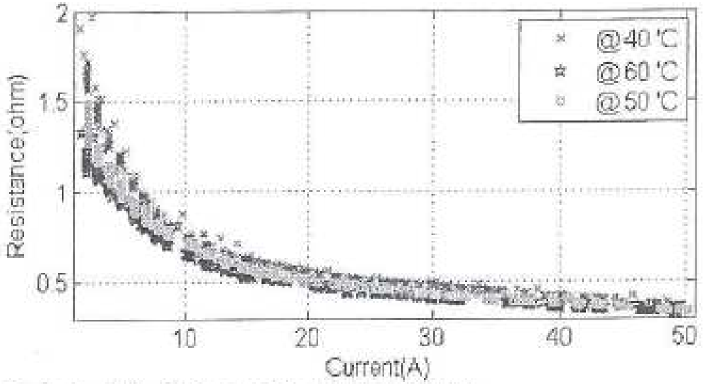

Fig. 2. the relationship between R_{in} and system current.

During experiments, this paper convincingly shows that both the stack temperature and the equivalent internal resistance of the Nexa^{TM} PEM power module have significant effects on the dynamic characteristics of the fuel cell output. A semi-empirical dynamic model for a Nexa^{TM} PEM power module considering the characteristics of the temperature and the equivalent internal resistance has been developed in the paper. This developed model has been validated using the experimental data. The results have persuasively shown that the developed model can accurately represent the Nexa^{TM} PEM power module in a wide range of load conditions. In addition the ultracapacitor dynamic model was used to supply the extra power required during peak demand periods. The parallel combination of the FC system and UC bank exhibits good performance for the stand-alone residential applications during the steady-state, load-switching, and peak power demand. Also, it can be extended for use in many areas such as portable devices, heavy vehicles, and aerospace applications. Without the UC bank, the FC system must supply this extra power, thereby increasing the size and cost of the FC system. The lifetime of a FC system can be increased if combined FC system and UC bank is used instead of a stand-alone FC system or a hybrid FC and standby battery system.

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