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Development of enhanced materials for direct-methanol fuel cell by combinatorial method and nanoscience

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Abstract

In this review we selectively summarize recent progress, in the development of the direct-methanol fuel cell (DMFC). The paper is mainly focused on research of electrocatalysts and electrolyte membranes, which are the important materials in DMFC that is a power generator to convert a chemical energy to electrical energy. However, in spite of a huge amount of work on these materials, there are still many obstacles that should be overcome for commercialization of DMFC. Here, we report the approaches of combinatorial method and nanoscience for developing electrocatalsyts and electrolyte membranes.

Keywords: Direct methanol fuel cell; MEA; Electrocatalyst; Membrane; Methanol

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1. Introduction

A schematic of a direct-methanol fuel cell (DMFC) is shown in Fig. 1. Methanol and water react to produce carbon dioxide, electrons and protons at anode (Eq. (1)). The electrons and protons, which are transferred via external circuit and electrolyte membrane, respectively, react with oxygen to produce water at cathode (Eq. (2)).

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \qquad (1)$$

$$\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \qquad (2)$$

The direct-methanol fuel cell is open considered to be the ideal fuel cell system because liquid methanol is used as a fuel. Other fuel cells (polymer electrolyte fuel cell, phosphoric acid fuel cell, solid oxide fuel cell and so on) operate on gas fuels such as hydrogen or hydrocarbons. However, poor performance of membrane-electrode assembly (MEA), mainly resulted from kinetic or activation over-potential at both anode and cathode, is a major limitation for commercializing DMFC [1].

Thin polymer membrane is not only used as an electrolyte allowing proton transfer in MEA but also acts as an electronic insulator and gas barrier between the two electrodes. Nafion^{TM} membrane is generally used for these purposes but it has some disadvantages such as high methanol crossover rate, resulting in cathode performance decay as well as fuel loss, and insufficient proton conductivity and thermal conductivity. The methanol crossover is caused by permeation of methanol due to a concentration gradient and by molecular transport due to electro-osmotic drag [2,3].

One way to solve these problems is to develop a new electrocatalyst and electrolyte membrane using combinatorial method and nanotechnology. Hence, in this paper, we selectively summarize recent progress, primarily from our research group, on these research categories.

2. Combinatorial chemistry

Combinatorial chemistry and high-throughput screening have had an enormous impact on the drug discovery in the pharmaceutical industry and are complementary technologies for the preparation of large numbers of formulations and their performance testing [4–6]. After nearly three decades of research and optimization, PtRu is one of the best-known

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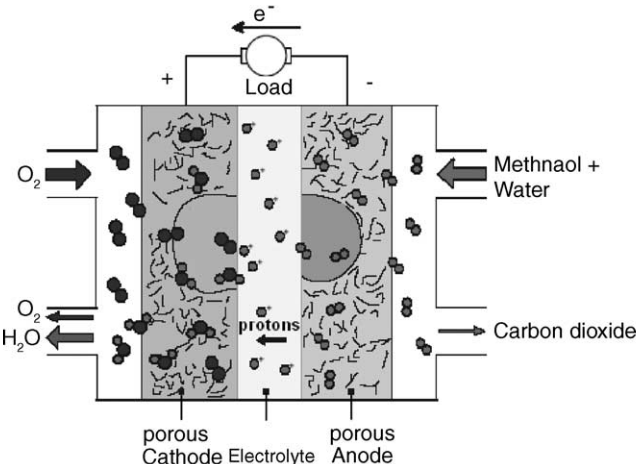

Fig. 1. Schematic of DMFC employing a solid polymer electrolyte membrane and electrodes [49].

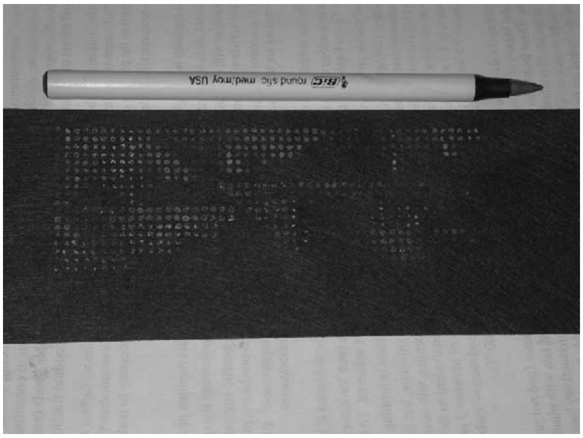

Fig. 2. Combinatorial array (645) synthesized using micro-liquid dispensing system.

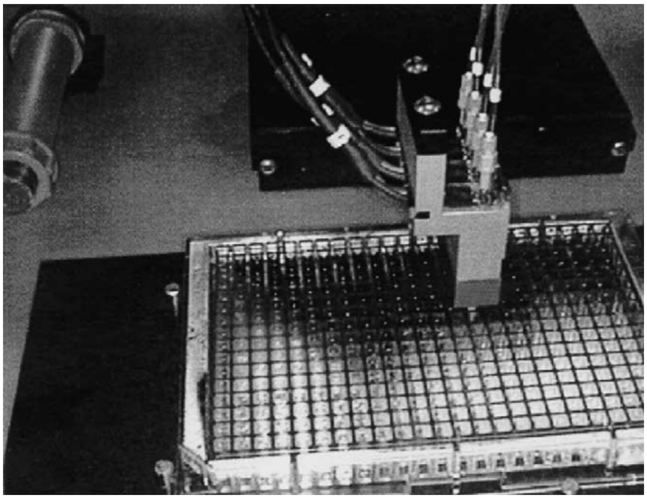

Fig. 3. The stock solutions, delivered from four metal precursor solutions, in a 384-well plate.

anodic materials [7–11], there still exists a need for methods providing the rapid assessment of many anode electrocatalysts of which compositions are all different.

In this area, Mallouk and his co-workers [12] first reported a combinatorial electrochemistry using fluorescence acid indicator such as acridine and quinine and that Pt(44)Ru(41)Os(10)Ir(5) is more active than commercial Pt(50)Ru(50) black in DMFC. Woo et al. [13] suggested a very active and stable quaternary electrocatalyst, Pt(77)Ru(17)Mo(4)W(2), which was found by high-throughput screening after a repeated cyclic voltammetry experiments. This method expanded the combinatorial electrochemistry using fluorescence indicators into a screening tool to find the catalyst that not only showing an initial excellent performance but also being active in the long-run reaction. However, because they used a calibrated ink-jet printer for synthesizing combinatorial library, it was very difficult to prepare the homogeneous phase in a dot of combinatorial array. Therefore, we now use a micro-liquid dispensing system and the as-prepared array containing 645 compositions is shown in Fig. 2. Before dispensing a solution of metal precursors on carbon paper, we prepared 645 stock-solutions in 384 well-plates and then they were treated in a ultrasonic bath for obtaining homogeneous phase (Fig. 3).

However, because it is not possible to detect the proton concentration in each combinatorial array using this method, Sullivan et al. [14] described an automated electrochemical analysis with combinatorial electrode arrays in a common electrolyte. Chu and Jiang [15] suggested another screening method which is able to measure the electrochemical properties of various electrodes in neutral, concentrated acidic and concentrated basic solutions.

Since the polymer membrane is a solid phase, it does not penetrate deeply into the electrode as does a liquid and the reaction area is limited to the contact surface between the electrode and membrane. To increase this contact surface area, ionomers like Nafion are impregnated into the catalytic layer [16,17]. Shul and his co-workers [17] reported combinatorial screening results to evaluate the influence of the Nafion ionomer in the PtRu alloy on the methanol electrooxidation using acid indicator.

In order to execute a combinatorial approach for discovery of novel electrocatalyst, DuPont has developed rapid half-cell screening techniques to evaluate catalyst activity for methanol oxidation and oxygen reduction [18]. Because these measurements are performed in liquid electrolyte and 32 electrodes can be screened in parallel in a 3-electrode configuration, it is possible to generate quantitative electrocatalytic activities using this experimental set-up.

3. Nanostructured electrocatalysts

In a DMFC, high-surface-area PtRu blacks have generally been used as an electrocatalyst [19]. However, current densities in the fuel cell do not scale with their intrinsic surface areas and metal loadings. This problem is complicated by the use of polymeric binders for incorporating the PtRu black powders into the desired electrode geometry [20]. Because this hindrance mainly results from the ineffective mass transfer and diffusion in a thick electrode layer that has numerous interfaces between randomly-shaped fine nanoparticles and polymeric binders, a three-dimensional PtRu nanostructured material can be used as a new electrocatalyst to enhance the performance of DMFCs.

As a method for nanostructured materials synthesis, replication has been the mainstay for molding novel material that is synthesized on various lengths and shapes in a removable template [21–23]. Woo et al. [24] prepared a PtRu nanowire network using SBA-15 nanoreactor and reported that this nanostructured material showed a higher performance than commercial PtRu black in DMFC, as shown in Fig. 4. Especially because Pt nanoclusters act as a hydrogenation catalyst in SBA-15 mesopores, Ru adatoms are evenly deposited on Pt using the reaction between the small Pt nanoclustes and $(NH_3)_6RuCl_3$ and well-defined PtRu bimetallic nanowire network can be synthesized.

Nanostructured platinum prepared by liquid phase template was reported as model electrocatalyst by Jiang and Kucernak [25]. It was synthesized using the chemical reduction of hexachloroplatinic acid dissolved in aqueous domains of the liquid crystalline phases of oligoethylene oxide surfactants. This nanostructured material showed a very low CO-poisoning rate at potentials relevant to fuel cell operation.

Another approach for nanostructured electrocatalyst deals with the development of carbon support materials [26], which can affect the size and shape of Pt particles. Because high price of Pt is one of main obstacles to prevent DMFC from being commercialized, supporting fine and uniform Pt particles on carbon support is very important. In developing a carbon support, many characteristics including surface area, pore size distribution, morphology and surface properties should be considered. First, high-surface area carbons are important for preparing an efficient electrocatalyst of fuel cells. However, because Pt particles supported on the highly porous carbon result in the thick electrode layer and can increase the internal resistance of membrane-electrode assembly (MEA), the surface area should be optimized in view of MEA preparation. Secondly, because the electrocatalysts are coated on gas diffusion layer using a polymeric binder such as Nafion or Teflon, their morphologies and pore size distributions should be controlled in the way of maximizing the electrochemical surface area. Thirdly, surface or bulk properties of carbon also affect the electrocatalytic activity. For example, hydrophilic and hydrophobic properties, proton spillover, electric conductivity and adsorption/absorption of CH_3OH and H_2O are studied in understanding the resulting activity.

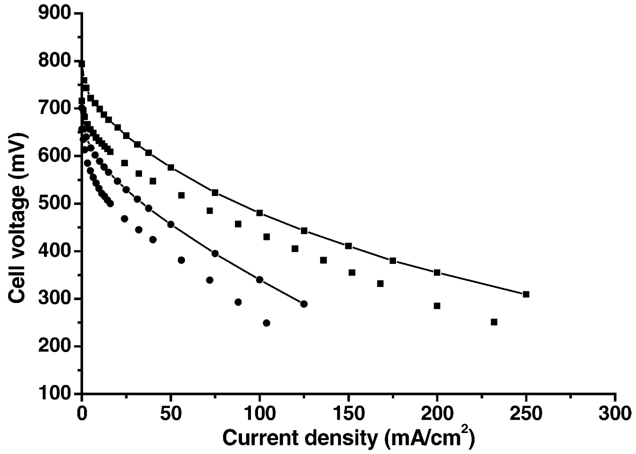

Fig. 4. DMFC current density–voltage curves at 40 °C (circles) and 80 °C (squares) comparing the performance of PtRu nano wire powder (connected data point) with that of Johnson Matthey commercial PtRu black (unconnected data point) in the single cell test (catalyst loading: 5 mg/cm^2).

For this purpose, considerable efforts have made in developing the Pt particles supported on nanostructured carbons [26,27]. The highly dispersed Pt clusters was obtained by using an ordered nanoporous carbon (CMK-5) and gave rise to promising electrocatalytic activity for oxygen reduction [26]. Baker and his co-workers examined three types of graphite nanofiber (GNF), “platelet”, “ribbon”, and “herring-bone” structures during electrocatalyzed methanol oxidation studies and demonstrated the improved mass activities of 5 wt.% Pt on platelet and ribbon type GNF [27]. Also, single-wall carbon nanohorns were reported to support fine Pt particles, which should be used for fuel cell application [28].

In order to prepare a nanostructured carbon having larger macropore (∼200 nm), Yu et al. [29] removed a colloidal silica as a template after polymerization of phenol and formaldehyde and its pyrolysis. PtRu supported on this mesoporous carbon showed a 15% higher power density than commercial catalyst, resulting from the higher surface area of the porous carbon and the three-dimensionally interconnected uniform macropores which favor efficient fuel and product diffusion. Hyeon and his co-workers [30] reported a carbon nanocoil (CNC) which was simply synthesized by heat-treating composites composed of a carbon precursor, silica, and a transition-metal salt. Resorcinol-formaldehyde gel and cobalt and nickel salts were used as a carbon precursor and catalyst precursor. In order to obtain a high-surface area carbon, a silica sol was added to the mixture to obtain carbon materials. In this procedure, carbon materials with high surface area as well as good crystallinity could be synthesized and its supported PtRu nanoclusters showed 170–230% higher power density than commercial catalyst. They suggested the superior performance of CNCs is resulted from the higher electrocatalytic activity for methanol oxidation, the low electrical resistance for current collection and the unique pore characteristics of the support, which favor the diffusion of methanol fuel and the removal of the by-product CO_2 gas.

4. Electrolyte membrane

Typically perfluorosulfonated polymer, Nafion™ has been used as a commercial polymer electrolyte membrane. It has the SO^{3-} side chains fixed at CF backbones. Due to its structure, the phase separation occurs between hydrophilic regions and hydrophobic ones in hydrated Nafion™. The hydrated protons move through the channels produced by this phase separation and Nafion™ can obtain high proton conductivity in the hydrated state. However, phase separation simultaneously gives the channels for methanol and water molecules transfer. Typically, in proton conducting polymer electrolyte, proton conductivity depends on the mobility of water molecules according to the vehicle mechanism $(H^+ \cdots (H_2O)_n)$. In addition, considerable amount of methanol move from anode to cathode in DMFC and this methanol cross-over reduces the performance of cell due to the mixed potential.

Alternatives to commercial polymeric proton conducting membranes include the inorganic hybrid membranes. Among them, a variety of simple blends of polymer and inorganic conductor have been investigated. Nafion™ was used as a template and the reactions for the incorporations of inorganic phases occurred in the ionic cluster of proton conducting polymer electrolyte membrane. In the latter case, ionic clusters of proton conducting polymer acted as a nanoreactor. Examples of inorganic phases were such as silicon oxide [31–34], ORMOSIL [35–39], metal oxide [40], metal phosphonate [41] and heteropolyacids [42].

Using sol–gel reaction, silicon oxide, ORMOSIL or metal oxide can be incorporated in proton conducting polymer electrolyte matrix with the SO_3^- acidic site as catalyst. Mauritz and co-workers have been studied on Nafion/ORMOSIL (TEOS: DEDMS (diethoxydimethylsilane)) and [silicone oxide] hybrid with IR [36], fluorescence probe method [37], SAXS [38], thermal and mechanical analysis methods [39]. Adjemian et al. investigated PEMFC operation from 80 °C to 140 °C with perfluorosulfonic acid silicon oxide composite membranes. They used the Aciplex™ as well as Nafion™ as template of sol–gel reaction [31]. Recently, Savinell et al prepared and investigated Nafion/[silicone oxide] in terms of solvent uptake, permeability and conductivity [33,34]. They evaluated the Nafion/[silicone oxide] as polymer electrolyte membrane for high temperature polymer electrolyte fuel cell and DMFC.

In our research group, using TEOS and a variety of organic silane agents, Nafion/ORMOSIL hybrid membranes were prepared and characterized in terms of solvent uptake, permeability and conductivity [43]. We investigated how these properties of membranes correlated to their characteristics such as hydrophilicity and morphology. According to this, we evaluated possibilities for various Nafion/ORMOSIL to be applied to PEMFC or DMFC operation.

Using TEOS and organic silane agent, we could prepare the Nafion/ORMOSIL hybrid membranes with a variety of hydrophilicity and morphology. As the number of functional groups increased, the more packed and crystalline structures were obtained. And the number of organic groups determined the hydrophobicity or hydrophilicity of membranes.

Sorption at equilibration with liquid solvent—water and methanol were investigated. Water uptakes were dominated by the hydrophilicity of hybrid membranes. On the other hand, methanol uptakes were determined by free or void volume of membrane. This is due to the difference of polarity between two solvents. Methanol permeability was correlated with the two solvent uptakes. Methanol permeation consisted of methanol sorption and methanol diffusion. The former was directly related to methanol uptake. In addition, methanol diffusion was more facile in higher wet porosity in methanol-water solvent. The type of organic groups in ORMOSIL as well as hydrophilicity and morphology affected proton conductivity. Nafion/[ORMOSIL (TEOS: TEVS(triethoxyvinylsilane)) had much lower proton conductivity. It can be seen that this features is due to the interactions between water, organic chain and proton. According to this work, by selecting the type and composition of organic silane agent, it is possible to control the properties of proton conducting polymer for the specific goal of fuel cell operation.

It could be incorporated with metal nanoparticles by ion exchanges of metal precursor ions with counter ions of SO_3^- group and it has been used as a support of metal catalysts [44,45]. Recently, Watanabe and his co-workers investigated Nafion-Pt nanoparticle composite membranes in order to self-humidified polymer electrolyte in PEMFC and to reduce the methanol permeability. In these studies, Pt nanoparticles acted as the nanoreactor in which water was produced via oxygen reduction or methanol was removed via methanol oxidation [46,47].

In our research group, palladinized Nafion™ was prepared via ion-exchange and chemical reduction method [48]. The type of palladium precursor determined the state of palladium cluster. In addition, solvent system determined the diffusion of ions from metal precursor due to the difference of swellability. Thereby, the tortuous thin Pd film was formed on the surface of membrane when Na^+-Nafion and water were used. This thin film reduced the methanol permeability significantly. Pd nanoparticles increased the water uptake of Nafion™ and reduced its methanol uptake. And dispersed Pd nanoparticles in Nafion™ disturbed the proton conduction and the methanol permeation simultaneously in Nafion™ cluster. In order to reduce the methanol permeation of Nafion™ and keep its conductivity high, it was more efficient for Pd nanoparticles to distribute near the surface of membrane. Palladinized Nafion™ improved the performance of DMFC single cell by reducing the methanol permeation (sorption and diffusion). Fig. 5 is I–V performances of MEA synthesized using PtRuMoW anode catalyst, of which composition was determined in combinatorial screening [13], and palladinized Nafion membrane [48].

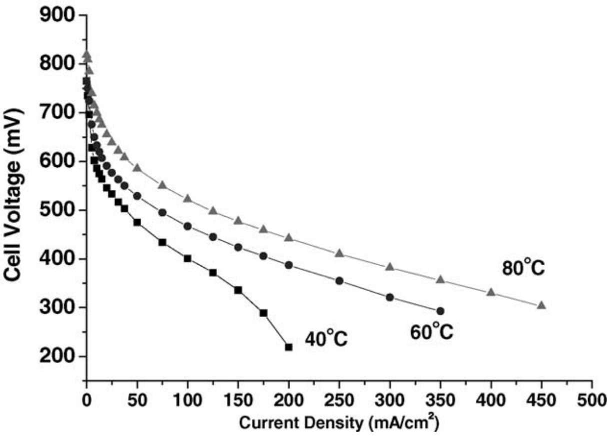

Fig. 5. DMFC current density–voltage curves at various cell temperature with 2 M methanol solution. Catalyst loading of anode and cathode was 5 ± 0.5 mg PtRuMoW [13] and commercial Pt black (Johnson Matthey, Hispec1000), respectively. The flow rate of methanol fuel and oxygen was 2 and 500 ml/min and palladinized Nafion membrane [49] was used as an electrolyte.

5. Conclusion

Even though from 1960 to now, the development of DMFC has been rapidly progressed, there are many technical problems to hinder its commercialization. Among them, the most challenging ones are the enhanced electrocatalytic activity of each electrode and the improved properties of electrolyte membrane. From these points of view, combinatorial chemistry and nanotechnology will take an important role in the development of DMFC. Only a few electrocatalysts, alternatives to Pt, have been proposed for methanol oxidation and oxygen reduction. High-throughput screening of combinatorial array that does not contain noble metals should be tested. The perfluorosulfonic acid polymer electrolyte such as Nafion is very expensive. There has been a lot of research on alternative proton conducting membranes but it is still a challenge to attain a sufficiently high specific conductivity and stability. Newly-developed nanocomposite membrane should have not only high proton conductivity and stability but also be applicable to the process for MEA fabrication.

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