Manganese based transition metal oxide catalysts for oxygen electrodes in fuel cells

Adlar Simmons^{*}, Jingsi Yang and Jun John Xu Department of Ceramic & Materials Science, Rutgers University, Piscataway New Jersey 08854

*Morehouse College (Atlanta, GA) for RISE@Rutgers, a summer research program that is for minority students and supported by the National Science Foundation.

Abstract

Fuel cells are efficient energy sources that convert chemical energy stored inside the fuel into electrical energy. They are environmentally benign in operation as no SO₂ or NO is produced. Potential markets include the automotive industry, computers, and wireless communications. Fuel cells have remained costly, however, because they incorporate expensive platinum catalysts to accelerate the oxidation reaction of fuels at the anode and the reduction reaction of oxygen gas at the cathode. Using precipitation methods, we attempted to synthesize catalysts out of more affordable amorphous manganese dioxide, both pure and doped with nickel. The amorphous manganese dioxide shows promising potential as an oxygen reduction catalyst for low power fuel cells. The effect of nickel doping on the catalytic performance manganese dioxide was investigated. The nickel-doped manganese oxide gives poorer performance than the pure amorphous manganese oxide because the average spacing of transition metal cations is changed and the catalytic ability is weakened as a consequence of this change.

Introduction

Although created in the early nineteenth century (Appleby and Foulkes, 1992; Kordesch, 1978), fuel cells that could produce significant energy were not developed until 1959 by Francis T. Bacon. Bacon's alkaline fuel cell, which was able to produce 5,000 watts, influenced the design of fuel cells that NASA later placed on the Apollo and Gemini spacecraft. Those fuel cells were astronomically expensive because of the amount of platinum needed. It was not until the 1980s and early 1990s that new designs allowed for the use of smaller quantities of the platinum catalyst. The Los Alamos National Laboratory (LANL), which is owned by the government (U.S. Department of Energy), contributed greatly to the advancements made.

Some potential applications of fuel cells include cars, portable power, and home electricity. If fuel cells were used in cars, the damage caused by exhaust to the atmosphere would be greatly reduced. Computers and other forms of portable communication could also benefit from the use of fuel cells. For example, a laptop

could run for up to twenty hours instead of the one-to-two hours typical with current rechargeable batteries.

A fuel cell works by combining a chemical fuel, usually hydrogen, natural gas, or methanol, with oxygen gas from the atmosphere. When hydrogen is used as the fuel, the operation of the cell produces only water and thus no pollutants.

Fuel cells (Wasmus and Kuver, 1999; Yuh et al., 1995) consist of two electrodes, an anode and a cathode, separated by an electrolyte, usually a liquid. Both the anode and cathode are coated with catalysts. At present popular catalysts are platinumruthenium alloy for the anode and platinum for the cathode. The function of the catalyst is to increase the rate of the reaction that occurs without itself being consumed. When hydrogen gas, for example, enters the anode, it is broken down into an electron and proton once the molecule comes into contact with the catalyst. If the fuel is something other than hydrogen, the chemical process will be much more complicated and the fuel will be broken into protons and other byproducts (Wasmus and Kuver, 1999). Electrons pass through the electrolyte to a negligible extent. The electrolyte functions only to allow the movement of charged ions. Protons travel through the electrolyte from the anode to the cathode under the influence of the electrical field between these two electrodes. The electrons produce electricity as they pass through an external circuit. At the cathode, the electrons combine with the protons and react with oxygen in the air to form water. Without this specific movement of ionic charge within the cell, the current would not flow.

To get useful current from the fuel cell, catalysts are required for both the hydrogen oxidation at the anode and the oxygen reduction at the cathode. So far platinum is the most efficient catalyst known for oxygen reduction, but platinum is scarce and costly. The challenge is to find a catalyst as efficient as but more economical than platinum. Oxides of manganese and of other transition metals, which are much more abundant and less expensive than platinum, are possible candidates. In this paper, amorphous manganese oxides and nickel-doped manganese oxides were synthesized by an oxidation route and their ability to catalyze the reduction of oxygen was tested.

Experimental methods

Manganese oxides and nickel-doped manganese oxides were obtained by the oxidation of manganese (II) chloride and nickel (II) chloride solutions by sodium hypochlorite (NaOCl) (Figure 1). First MnCl₂ was dissolved in 100 mL water to get 0.3 M solution. NiCl₂ was added to separate portions of the MnCl₂ solution to obtain Ni/Mn molar ratios of 0, 0.1 and 0.25 respectively. The mixtures were then slowly poured into 1.4L of 0.08M NaOCl. Prior to mixing the two solutions, the pH of the NaOCl solution was increased to 12 by the addition of 2M NaOH. The increase in pH is necessary to ensure that a pH of about 5 is reached after the addition of the manganese solution. After the two were mixed, the solution was stirred for two hours to allow all of the particles to disperse evenly. Finally, the solution was left to settle

for twenty-four hours. The precipitate that forms is MnO_2 with nickel cations in its structure.

The precipitate was separated from solution by pouring off the supernatant, and by dialyzing the remaining slurry against deionized water. During dialysis, the water was changed at intervals of one, four, eight, sixteen, twenty-four, and forty-eight hours. The precipitate was then removed from the dialysis tube and prepared for centrifuging. After centrifuging for ninety minutes, the samples were freeze dried.

Slurry was prepared from the freeze-dried samples by adding water, a high surface area amorphous carbon powder, and PTFE (polytetraflouroethylene) binder, which binds the sample and the carbon. The manganese oxide and carbon powder together make up 85wt% of the electrode slurry. The other 15wt% consists of the PTFE binder. Specifically, carbon powder was first mixed with the active material (manganese oxides or nickel-doped manganese oxides). Second, water was added and the slurry was stirred for 10 minutes. Third, the PTFE binder was added and the slurry stirred for an additional hour. Finally, the slurry was applied to the carbon paper, which functions as both the catalyst substrate and the current collector.

We made "testing electrodes" in two ways (Kordesch et al., 1984). The first was to apply the slurry to the carbon paper with a brush for a total of twenty coats. Between coats, the sample was placed in an oven to dry at 75 °centigrade. The second method was to apply the slurry onto the surface of the carbon paper and then to pass both the carbon paper and the half-dried slurry through a Roll Mill. The sample was then placed in a hydraulic press under a pressure of one ton. Finally, the electrode was placed in a half-cell.

The testing cell consists of three electrodes and an electrolyte membrane. The three electrodes are designated the auxiliary, working, and reference electrodes. A platinum sheet is attached to the auxiliary electrode and conducts the current. Oxygen gas is led into the cell from the back of the working electrode and meets catalysts by passing through the porous carbon paper (Figure 2). The reference electrode is used to generate a standard reference potential. The electrolyte is 1N KOH aqueous solution. Once the testing cell is built, the electrodes are connected and ready for computer controlled testing. During the testing, a voltage was applied between the working electrode and the reference electrode, and the current was measured between the working electrode and the auxiliary electrode. The current indicates how much oxygen is catalytically reduced.

Results and discussion

The chemical reaction for our synthesis of manganese dioxide synthesis is shown in Equation 1.

$$MnCl_2 + 2NaOH + NaOCl \rightarrow MnO_2 + 3NaCl + H_2O \qquad (1)$$

If there are other transition metal ions such as nickel ions in the reaction solution, those transition metal ions will be trapped inside the structure of the manganese oxide. Thus the nickel-doped manganese oxides are synthesized.

The manganese oxide and nickel-doped manganese oxides synthesized are named NMO0, NMO1 and NMO2 according to the initial Ni/Mn molar ratios of 0, 0.1 and 0.25 respectively.

The kinetics and mechanisms of oxygen reduction have been investigated (Kinoshita, 1992) with a wide range of cathode materials and in a variety of aqueous electrolytes. For our current 1N KOH alkaline electrolyte, the reaction of oxygen reduction may proceed by two pathways (Kinoshita, 1992).

1. Direct 4-Electron Pathway

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-$$
(2)

2. Peroxide pathway

$$O_2 + H_2O + 2e \rightarrow HO_2^- + OH^-$$
 (3)

3. Followed by the decomposition of peroxide

$$2HO_2^- \rightarrow 2OH^- + O_2$$
 (4)

Rates of these reactions are very low. But in the presence of catalyst, the reaction rate can be enhanced by orders of magnitude. It is believed that these reactions happen on the surface of the catalyst. The nature of the surface on which the oxygen gas and the electrolyte meet and react is critical. The more reaction sites, the more oxygen will be reduced and the more current produced. One practical electrode, the planar electrode, is designed in such a way that the electrolyte is supplied from one side and the oxygen gas from the other side. Both the electrolyte and the oxygen gas penetrate into the electrode though channels existing inside the electrode and react with each other on the surface of the catalyst particles of the electrode.

Figure 3 shows scanning electron microscopy (SEM) images of the microstructure of the manganese oxide (NMO0). From Figure 3a, it can be seen that the manganese oxide powders are \sim 50µm in size. At a higher magnification of 10,000x, the nonporous structure of the manganese oxide is revealed. The manganese oxide powder is actually made up of solid networks of manganese oxides and pores around the size of 100 nm. Such nanoporous morphology is favorable to the oxygen reduction reaction because it supplies channels with enormous surface areas to let both the oxygen gas and the electrolyte meet with each other and react.

The X-ray diffraction pattern of the manganese oxide (NMO0) (<u>Figure 4</u>) indicates the structure of this sample. The small continuous peaks are evidence of

incomplete crystallization. Therefore, the manganese oxide sample is somewhat crystalline but mostly amorphous. We speculate that the manganese cations in this amorphous manganese oxide will be in a higher energy state and may therefore have greater catalytic activity.

The electro-catalytic performance of the amorphous manganese oxide and the nickel-doped amorphous manganese oxides are shown in Figure 5. The undoped amorphous manganese oxide has an open circuit potential of around 0.05 V vs. Normal Hydrogen Electrode (NHE). When the applied voltage is -0.45 V, the oxygen reduction current reaches around 40 mA/cm². This value is still several times lower than that of platinum electrodes (Han et al., 2000). But considering the huge difference between the cost of the manganese oxide and platinum, the amorphous manganese oxide has promising potential for applications in fuel cells for low power systems, e.g. portable devices, micropower generators, etc.

When nickel cations are introduced into the amorphous manganese oxide, we observed that the oxygen reduction current at the same applied voltage decreased with the increasing concentrations of nickel dopants. One likely reason is that nickel doping changes the atomic spacing of the manganese oxide and decreases the dissociative adsorption ability of the manganese oxide.

$$M^{z} \longrightarrow M^{z+1} \longrightarrow M^{z+1} \longrightarrow M^{z} \longrightarrow M^{z} \longrightarrow M^{z+1} \longrightarrow M^{z+1} \longrightarrow M^{z} \longrightarrow M^{z$$

Here one of the interactions for oxygen on the electrocatalyst surface of transition metal oxide is described in Equation 5 (Kinoshita, 1992). For the catalytic oxygen reduction reaction to occur, molecular oxygen is first absorbed laterally on two adjacent metal ions on the surface of the transition metal oxide. The O-O bond is lengthened and weakened by the metal-oxygen interaction. The dissociative adsorption of O_2 happens simultaneously with proton addition and an increase in the valence of the transition metal. This step is then followed by the reduction of the transition metal ions ($M^{z+1} \rightarrow M^z$) to regenerate the catalyst site. The spacing of transition metal atoms is critical for the catalytic reaction because it decides the extent that the O-O bond is weakened. For our case, we speculate that nickel doping modifies the average spacing of cations at the transition metal in such a way that the O-O bond is not weakened as much as in the absence of Ni. Thus the overall catalytic performance of the nickel doped amorphous manganese degrades with the concentration of nickel concentrations.

Conclusion

By using precipitation methods, we attempted to synthesize out of affordable manganese oxides economic catalysts for fuel cells. The manganese oxide synthesized by an oxidation route has a nanoporous microstructure and is mostly in an amorphous state. The electrocatalytic oxygen reduction reaction shows that pure amorphous manganese oxide has promising potential as oxygen reduction catalysts for low power fuel cells. The nickel-doped manganese oxide gives poorer performance than the pure amorphous manganese oxide. It seems likely that the nickel doping modifies the average spacing of transition metal cations and weakens the catalytic ability.

References

Appleby A. J., Foulkes F. R. (1992), Fuel Cell Handbook, Van Nostrand Reinhold, New York, 3-13.

Kordesch K. V. (1978) 25 Years of fuel cell development (1951-1976), Journal of the Electrochemical Society, 125, 77C-91C.

Wasmus S., Kuver A. (1999) Methanol oxidation and direct methanol fuel cells: a selective reviews, Journal of Electroanalytical Chemistry, 461, 14-31.

Yuh C., Johnsen R., Farooque M. and Maru H. (1995) Status of carbonate fuel cell materials, Journal of Power Sources, 56, 1-10.

Kordesch K., Jahangir S. and Schautz M. (1984) Engineering concepts and technical performance of oxygen-reducing electrodes for batteries and electrochemical processes, Electrochimica Acta, 29, 1589-1596.

Han E., Eroglu I. and Turker L. (2000) Performance of an alkaline fuel cell with single or double layer electrodes, International Journal of Hydrogen Energy, 25, 157-165.

Kinoshita K. (1992) Electrochemical Oxygen Technology, John Willey & Sons, Inc., New York, 19-29.



Figure 1: Synthesis of amorphous manganese oxides and nickel-doped manganese oxides.

Figure 2: Testing cell.



Figure 3: Microstructure of the amorphous manganese oxide.



a) 200x magnification



b)10,000x magnification

Figure 4: X-ray diffraction pattern of the amorphous manganese oxide.



Figure 5: Catalytic performance of nickel doped manganese oxides.



a) 200x magnification



b)10,000x magnification

Copyright 2002 by Jun John Xu