

Electrocatalyst Research for Low Temperature Fuel Cells

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) have received considerable attention for various applications (portable, mobile and stationary) due to their high energy densities, low operating temperature, low polluting emissions, and long life times [1-3]. The manufacturing costs, which arise mainly from the bipolar plates, the polymer electrolyte membrane, and the gas diffusion electrodes containing the electrocatalysts, are however a major problem to solve before PEFC technology becomes commercial attractive.

At the Institute of Electrochemical Process Engineering at Mannheim University of Applied Sciences, several topics on the electrocatalysis and reaction engineering for PEFC with hydrogen and reformat as fuel gas, as well as for the Direct Methanol Fuel Cell (DMFC) were studied:

- Anode electrocatalysts with high CO tolerance based on Platinum-Ruthenium [4]
- CO mitigation by addition of dilute hydrogen peroxide solution to the fuel gas stream [5]
- Fundamental research on the influence of hydrogen peroxide on the adsorption and oxidation of CO, methanol and ethanol [6,7]
- Cathode catalysts for the DMFC based on Platin alloys [8]

The best electrocatalyst for oxygen reduction in low temperature PEFCs is Pt or Pt alloys dispersed on carbon. However, Pt is expensive and has a limited availability. One option to reduce the electrode costs is to increase Pt utilization and reduce Pt loading. Replacing Pt with a relatively inexpensive nonnoble-metal-based electrocatalysts is another possibility. Therefore, N₄-macrocycles were tested in a joint project between Mannheim University of Applied Science and Jiao Tong University.

2. Electrocatalyst for Direct Methanol Fuel Cells based on CoTmPP

The search for efficient and low cost electrocatalysts for cathodic oxygen reduction other than Pt and Pt-alloys has been intensive investigated because of their importance in applications for PEFC and also for alkaline system such as the metal/air batteries [9-11]. In last few years, several transition metal organic macrocycles (N₄ - metal chelates) [12] adsorbed on carbon have been proposed to catalyze the oxygen reduction reaction (ORR) selective catalyst. Prominent among them are N₄ - macrocycles based on a metal containing porphyrin system (e.g. Cobalt-Tetramethoxyphenylporphyrin, CoTMPP [13]), chevrel phase type compounds (e.g., Mo₄Ru₂Se₈) and other transition metal chalcogenides (see [14] and references therein).

Microwave synthesis method was applied to prepare Cobalt-Tetramethoxyphenylporphyrin (CoTMPP) supported on Black Pearls 2000 and Vulcan XC 72R. The influence of chemical pretreatment by 6 mol dm⁻³ HNO₃ and 30 wt % H₂O₂ on the activity of electrocatalysts for oxygen reduction was investigated by means of cyclic voltammetry and rotating disc electrode technique. Three types of electrolytes (0.5 mol dm⁻³ H₂SO₄, 0.5 mol dm⁻³ H₂SO₄ / 0.5 mol dm⁻³ CH₃OH or 1 mol dm⁻³ KOH) were used. It was found that electrocatalysts prepared by microwave method show higher activity for oxygen reduction compared with normal organic flux synthesis method. After chemical pretreatments of carbon support, the oxygen reduction activity of CoTMPP was improved largely improved significantly. It is interesting to note that electrocatalysts have better activity of oxygen reduction in 0.5 M H₂SO₄ / 0.5 mol dm⁻³ CH₃OH than in pure sulfuric acid electrolyte. Finally, membrane electrode assemblies with a CoTMPP cathode for Polymer Electrolyte Fuel Cells (PEFC) were fabricated and tested.

3. Conclusions

Heat treatment of carbon support under Argon atmosphere at 900 °C is necessary to improve the activity and stability of CoTMPP based electrocatalysts.

Black Pearls 2000 should be the better support than Vulcan XC 72R as carbon because of its larger BET and less average particle size. Both CoTMPP on Black Pearls 2000 and on Vulcan XC 72R prepared the microwave method have good catalytic activity for oxygen reduction. Carbon supports chemical pretreated with 6 mol dm⁻³ HNO₃ and 30 % H₂O₂ greatly improved the activity. Furthermore, chemical pretreatment of carbon supports with H₂O₂ show advantages compared to HNO₃ pretreatment due to more surface groups like hydroxy groups (-OH) produced on carbon surface. This improves the adsorption and distribution of metals and oxides on the support.

The activity of electrocatalysts in 0.5 mol dm⁻³ H₂SO₄ + 0.5 mol dm⁻³ CH₃OH solution is much more better than that of in 0.5 mol dm⁻³ H₂SO₄. The electrocatalysts prepared in this work hope to solve the problem which catalysts losing activity because of CH₃OH penetration in DMFC.

The number of transferred electrons during of oxygen electroreduction on CoTMPP cathodes is found to be between 2 and 4 giving evidence for the production of hydrogen peroxide.

The fabrication of membrane electrode assemblies useful in polymer electrolyte fuel cells based on carbon supported CoTMPP is presented. It was found that the cell performance using cathodes based on supported Pt are still higher than CoTMPP cathodes. However, the excellent performance of electrocatalysts in 0.5 mol dm⁻³ H₂SO₄ + 0.5 mol dm⁻³ CH₃OH need further investigation. In this way, methanol tolerant cathodes could be formed suitable for DMFC applications.

4. References

1. Prater, K.B., 1992, *J. Power Sources*, vol. 37, pp. 181.
2. Appleby, A.J., 1994, *Int. J. Hydrogen Energy*, vol. 19, pp. 175.
3. Schlesmith, J.P., Collins, R.D., Oakley, M.J., and Stevenson, D.K., 1994, *J. Power Sources*, vol. 49, pp. 129.
4. Oetjen, H.F., Schmidt, V.M., Stimming, U., and Trila, F., 1996, *Electrochem. Soc.*, vol. 143, pp. 3838.
5. Barz, D.P.J., and Schmidt, V.M., 2001, *J. Phys. Chem. Chem. Phys.*, 3, pp. 330.
6. Schmidt, V.M., Rodriguez, J.L., and Pastor, E., 2001, *J. Electrochem. Soc.*, vol. 148, pp. A 293.
7. Schmidt, V.M. et al., 2006, *J. Appl. Electrochem*, DOI 10.1007/s10800-006-9178-z.
8. Drillet, J.F., and Schmidt, V.M. et al., 2002, *Electrochim. Acta*, vol. 47, pp. 1983.
9. Yeager, E., 1984, *Electrochim. Acta*, vol. 29, pp. 1527.
10. Kinoshita, K., 1992, *Electrochemical Oxygen Technology*, Wiley, New York.
11. Matins, A.M.C., Dodelet, J.P., Guay, D., Ladouceur, M., and Tourillon, G.J., 1992, *Phys. Chem*, vol. 96, pp. 10898.
12. Zagal, J.H., 2003, in Vielstich, W., Gasteiger, H.A., and Lamm, A., Eds., *Handbook of Fuel Cells—Fundamentals, Technology and Applications*, vol 2: Electrocatalysis, Chichester, Wiley & Sons, pp. 543.
13. Bogdanoff, P. et al., 2004, *J. New Mater, Electrochem. Syst.*, vol. 7, pp. 85.
14. Alonso-Vante, N., 2003, in Vielstich, W., H.A., Gasteiger, Lamm, A., Eds., *Handbook of Fuel Cells*, vol 2: Electrocatalysis, Chichester, Wiley & Sons, pp. 534.

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Author Biography

Prof. Dr. V.M. Schmidt is Head of the Institute of Electrochemical Process Engineering in the Faculty of Process engineering and Chemical Technology. Born in 1960, he studied Chemistry at the University of Bonn and got his Ph.D. in 1991 at Private University of Witten/Herdecke. After a post-doc at Prof. Vielstich's group in Bonn 1990—91, he was project leader for low temperature fuel cell at Research Centre Jülich, Germany (1992-1997). Between 1995 and 1998, Dr. Schmidt was the German representative in a working group of the International Energy Agency (IEA) on low temperature fuel cells. Since 1997, Dr. Schmidt is at Mannheim University of Applied Sciences teaching physical chemistry and electrochemical process engineering. His research is focused on electrocatalysis for fuel cells and batteries and on the reaction engineering of electrochemical processes.