A Novel Air Electrode Based on a Combined Use of Cobalt Phthalocyanines and Manganese Oxide

Takeo Ohsaka*, Kazuki Arihara*, Lanqun Mao*, Paul A. Liddell**, Ernesto Marino-Ochoa**, Ana L. Moore**, Tatsuya Imase*, Dun Zhang* and Tadashi Sotomura***

*Department of Electronic Chemistry, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

**Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604, USA

*** Advanced Technology Research Laboratories, Matsushita Electric Ind. Co. Ltd., 3-4 Hikaridai, Soraku-gun Seika-cho, Kyoto 619-0237, Japan

An efficient air electrode has been one of the most important issues concerning metal-air batteries and fuel cells. At present, platinum (Pt) or its alloy supported on nanometer-sized carbon particles is the most efficient catalyst for the reduction of dioxygen (O_2) to water by transferring four electrons at a time. However, because the Pt catalysts still have problems including high cost and lack of selectivity toward crossover fuels, numerous papers have been dedicated to designing an innovative catalyst for the electrocatalytic reduction of O_2, which can replace the Pt catalysts.

Transtion metal macrocyclic complexes such as phthalocyanines and porphyrins have been the candidates for the cathode catalyst of air electrodes. Most of these complexes generally accelerate the two-electron reduction of O_2 producing hydrogen peroxide except for a few iron phthalocyanines and co-facial metal diporphyrins. For example, cobalt phthalocyanine (CoPc) is known as such a catalyst, leading to 50 % of the theoretically available power utilized in H_2/O_2 fuel cells with CoPc-modified electrodes. But the disastrous production of hydrogen peroxide has been main reason for the abandonment of the application of CoPc as an electrocatalyst for the O_2 reduction.

A novel strategy to solve the above-mentioned problems is a combination of two stable catalysts for the efficient O_2 reduction: one is an electrocatalyst for the two-electron reduction of O_2 to hydrogen peroxide and the other is a catalyst for the chemical decomposition of hydrogen peroxide to water [1-3]. Recently we have proposed an elaborate catalytic system using phthalocyanine and manganese oxides that are stable and less expensive. Among the manganese oxides, MnOOH acts as the best catalyst for the disproportionation reaction of hydrogen peroxide into molecular oxygen and water. In the present work, we adopted phthalocyanines with the electron-withdrawing substituents as the electrocatalyst for the two-electron reduction of O_2 and examined these catalytic systems combined with MnOOH [4]. This combination effects the electro-reduction of O_2 through the two-electron step and subsequent chemical decomposition of HO_2^-. The four-electron reduction of O_2 was evident from the almost twofold increases of the cathodic current in CVs and the steady-state current in rotating ring-disk electrode (Fig, 1), the collection efficiency *N*, and the number of electron *n* calculated from the K-L plot. The catalytic activity for O_2 reduction at the MnOOH and CoPcCN modified electrode was greatly improved in comparison with the bare GC electrode; its performance is not far from that of a Pt electrode. Further improvement would be expected by adequate application of electrocatalysts with MnOOH.

References:

1. L. Mao, T. Sotomura, N. Koshiba, D. Zhang and T. Ohsaka, *J. Electrochem. Soc.*, **149**, A504 (2002).
2. L. Mao, K. Arihara, T. Sotomura and T. Ohsaka, *Chem. Commun.*, 2818 (2003).
3. L. Mao, D. Zhang, T. Sotomura, K. Nakatsu, N. Koshiba and T. Ohsaka, *Electrochim. Acta*, **48**, 1015 (2003).
4. K. Arihara, L. Mao, P. A. Liddell, E. Marino-Ochoa, A. L. Moore, T. Imase, D. Zhang, T. Sotomura and T. Ohsaka, *J. Electrochem. Soc.*, in press.

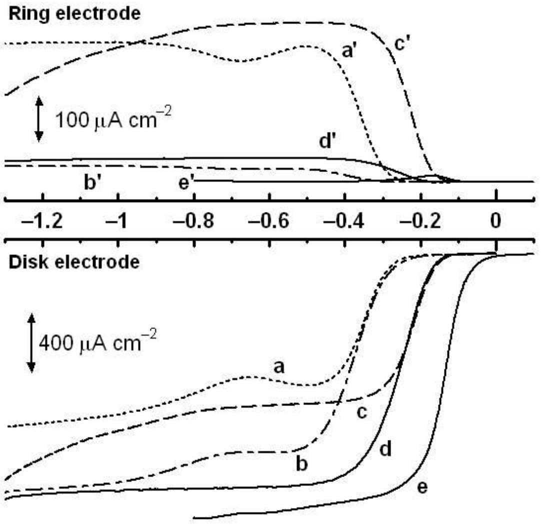

Fig. 1. RRDE voltammograms of GC (or Pt)-disk and Pt-ring electrodes obtained in 0.1 M KOH under O_2 atmosphere. The disk electrodes were Nafion/GC (a and a'), Nafion-MnOOH/GC (b and b'), Nafion/CoPcCN/GC (c and c'), Nafion-MnOOH/CoPcCN/ GC (d and d') and Nafion/Pt (e and e'). The ring electrode potential was kept at +0.5 V. Scan rate was 0.01 V s^{-1}. Rotation rate was 200 rpm.