Mesoporous Pt-Carbon Nanocomposite arrays as a methanol-tolerant cathode material of DMFC

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The "methanol crossover" through an electrolyte membrane from anode to cathode is one of the most practical problems limiting the performances of the direct-methanol fuel cell (DMFC)[1]. During DMFC operation, the anode performance is increased with increasing methanol concentration but the methanol crossover rate is also increased, causing degradation of the cathode performance[2]. Although development of methanol-tolerant oxygen reduction electrocatalysts such as transition metal sulfides and $Ru_{1.92}Mo_{0.08}SeO_4$ is a promising approach[3], platinum electrocatalyst is generally used because of its high stability in acidic and high over-potential conditions.

Regularly interconnected PtC nanocomposite arrays containing Pt clusters mostly less than 0.9 nm inside wall, which are exposed to the mesopore through micropores in the wall, were synthesized by using mesoporous silica (SBA-15) templating method.

In order to confirm the methanol-tolerant characteristic of PtC nanocomposite in real fuel cell system, open-circuit voltages (OCV) of DMFC single cells using PtC nanocomposite and commercial Pt/C (EC-20-PTC) as a cathode are shown in Fig. 1. At various methanol concentrations and cell temperatures, the OCV of PtC nanocomposite are 40~60 mV higher than those of commercial Pt/C. Current density of PtC nanocomposite was higher than that of EC-20-PTC at an activation polarization regime. In the case of 2M methanol at the anode, the current density of PtC nanocomposite (67 mA/cm^2) was 180% higher than that of EC-20-PTC (36 mA/cm^2) at 810 mV [RHE]. For 4M methanol at the anode, the current density of PtC nanocomposite (56 mA/cm^2) was 370% higher than that of EC-20-PTC (15 mA/cm^2) at 800 mV [RHE]. Higher OCV and current densities indicate that PtC nanocomposite is more methanol-tolerant than EC-20-PTC. Fig. 2a and b show the oxygen reduction activity of PtC nanocomposite and EC-20-PTC in the O_2-saturated 1M $HClO_4$ electrolyte with methanol. Electrooxidation of methanol by PtC nanocomposite is almost not observed between 850 and 1000 mV [NHE]. However, EC-20-PTC shows the electrooxidation activity of 50A/g Pt in 1M $HClO_4$/2M CH_3OH electrolyte at 1000 mV [NHE]. The ratio of the most active Pt(110) plane for methanol oxidation to Pt(100) and Pt(111) planes decreases with a decrease in a Pt particle size[4] and the mass activity for oxygen reduction reaches a maximum when there is the largest fraction of Pt(100) and Pt(111)[5]. Therefore, the methanol-tolerant property of the PtC nanocomposite is related to the characteristic orientation of ultrafine Pt nanoprticles (<0.9 nm) which are stabilized by strong Pt-C interaction.

References

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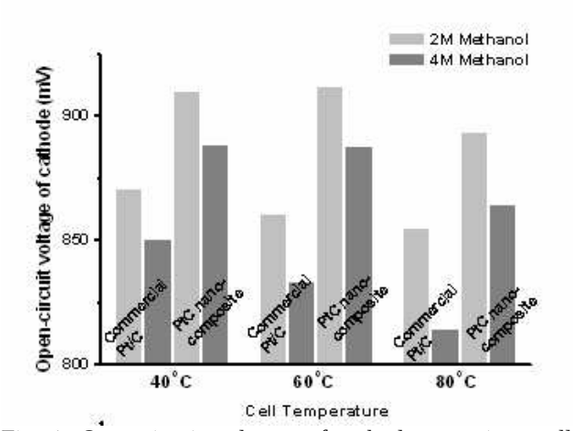

Fig. 1. Open-circuit voltages of cathode at various cell temperature and methanol concentration at anode

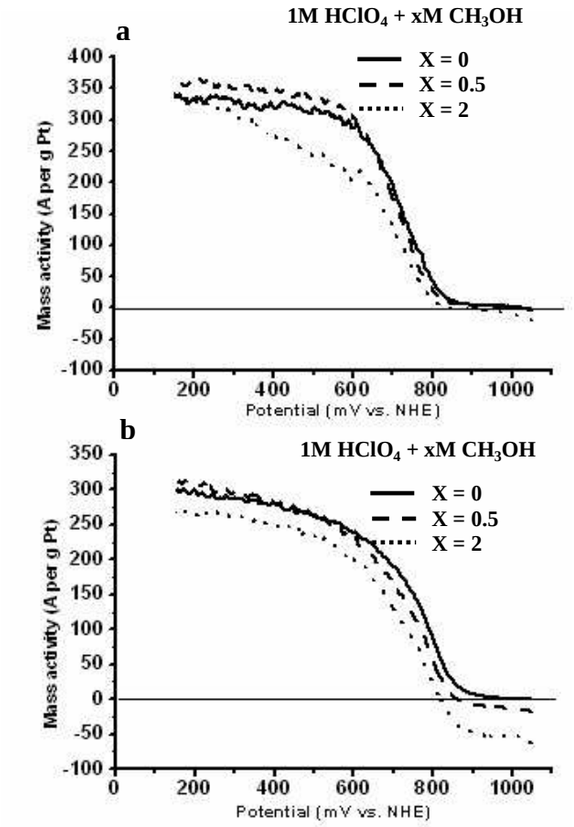

Fig. 2. Electrocatalytic mass activity of 12 wt% PtC nanocomposite (**a**) and commercial 20 wt% Pt/C (Electrochem, Inc., EC-20-PTC) (**b**) for the oxygen reduction in oxygen-saturated 1M $HClO_4$ with xM CH_3OH (x = 0, 0.5 and 2).