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Chakraborty , Debasish; Chorkendorff, Ib; Johannessen, Tue

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Metamorphosis of the Mixed Phase PtRu Anode Catalyst for Direct Methanol Fuel Cells After Exposure of Methanol: In-situ and Ex-situ Characterizations

D. Chakraborty, I. Chorkendorff, and T. Johannessen

Center for Individual Nanoparticle Functionality (CINF),
Dept. of Chemical Engineering and Dept. of Physics
Technical University of Denmark, Dk-2800, Kgs.
Lyngby, Denmark

In a recent article published in the Journal of the Electrochemical Society,¹ we discussed a novel one step method for the preparation of Pt-Ru anode electrode for direct methanol fuel cell (DMFC) by using flame spray pyrolysis (FSP). In this process, after dissolving Pt and Ru-precursors in appropriate solvents, the solution is sprayed through a nozzle to produce micron-sized droplets which burns out in a flame resulting in metal atoms and/or metal oxide molecules in the gas phase. Hereafter, clusters immediately nucleate and grow to nano-sized particles by coagulation and/or surface reaction and sintering. The mechanism of the particle formation process in the gas phase ensures intimate mixing of the product components. The product particles were collected directly on the Toray TGPH090 gas diffusion layer (GDL) by withdrawing the aerosol nanoparticles from the flame through it by using a gas-jet vacuum pump. Here, the GDL was, in principle, applied as a catalyst nanoparticle filter.

The X-ray diffraction (XRD) patterns of the deposits showed only the characteristic peaks of the face-centred cubic (fcc) crystalline structure of Pt. However, the lattice parameters (a_{fcc}) showed a very insignificant gradual decrease with increasing Ru content. The absence of any other crystalline phase leads us to envisage the flame prepared catalysts as a mixture of a crystalline phase consisting predominately of Pt and one or more amorphous phases consisting of mainly Ru as metallic or oxidic states. X-ray photoelectron spectroscopy (XPS) evidence suggested that both Pt and Ru existed mostly as oxides. The surface concentration of Pt and Ru estimated from the intensities of Pt and Ru peaks gives Pt atomic fraction of 0.48. However, the average of Pt atomic fraction determined from energy dispersive X-ray spectroscopy (EDS) was 0.58 ± 0.03 . Considering the fact that XPS signals mainly come from the surface and EDS signals primarily come from the bulk, the difference between the Pt atomic fraction determined from XPS and EDS, could be rationalized by postulating a thin amorphous surface layer consisting of Pt-Ru oxides on top of the nano-crystalline Pt fcc phase. The methanol electrooxidation activity of the mixed phase anode was compared with that of 10% PtRu/C catalyst from E-TEK. Both the catalysts were 50 atomic % Pt and same amount of catalysts were used for fabricating the membrane electrode assemblies (MEA). The E-TEK PtRu/C catalyst was chosen for comparison because of its higher degree of alloying compared to the flame synthesized mixed phase catalyst. The comparison showed a similar onset potential for both the anodes. However, the current was higher at higher potentials for the mixed phase catalyst.¹ The result is interesting considering the debate about the role of oxides in PtRu anode catalyst. While an overwhelming majority of the researchers believe that oxides are harmful, according to Rolison et al. the presence of oxides enhances the performance of DMFC

anode.² However, it is well known that both the physical and chemical properties of the anode catalysts changes with the exposure of methanol and during operation. Keeping this in mind, we studied the possible metamorphosis of the mixed phase anode catalyst in-situ by cyclic voltammetry (CV) and impedance spectroscopy. The anode compartment of a single cell was fed with methanol whereas the cathode, acted as a dynamic hydrogen electrode, was fed with hydrogen. The treatment was performed at two different temperatures; 50°C and 90°C. It was observed from the complex plane plots of the impedance measurements that the charge transfer resistance for methanol oxidation decreased monotonously with time before reaching a pseudosteady state. The decrease of charge transfer resistance was accompanied by an increase in reaction rate observed by the increasing current in the CV. However, the treatment at 90°C was more efficient not only requiring shorter time for reaching to the pseudosteady state, but also showing much higher current compared to the sample treated at 50°C (Fig. 1).

The two treated anodes were separated from the MEAs for performing XRD to figure out the difference with the virgin sample. The values of a_{fcc} extracted from XRD were 3.92, 3.88 and 3.86 for the virgin sample, sample treated at 50°C and sample treated at 90°C, respectively. The conclusion from the above results is that with the exposure of methanol, the mixed oxides are reduced to form PtRu alloy particles, and therefore, the higher activity of the flame prepared mixed phase PtRu anode is not possibly due to the presence of oxides in the sample. The faster kinetics of surface reduction at 90°C compared to 50°C is possibly the reason for higher degree of alloying at higher temperature. The higher degree of alloying could be responsible for the increase in current for the sample treated at 90°C.

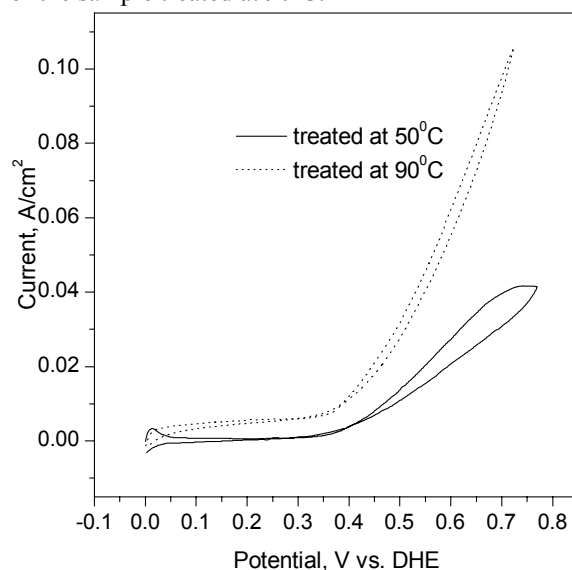


Fig. 1. CV with 1M methanol at 50°C of anodes treated at two different temperatures. Anode: $\sim 0.3 \text{ mg/cm}^2$ PtRu, Cathode: $\sim 2 \text{ mg/cm}^2$ Pt, Scan rate: 5 mv/s.

References

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