Pt-Ru Sputtered layer for Anode Surface Modification in Direct Methanol Fuel Cells

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Introduction

A sputtering technique for fabricating an ultra-thin catalyst (Pt) layer was employed in direct methanol fuel cells (DMFCs) [1] in our study [2]. However, the Pt sputtered layer on the Nafion® increased the cell ohmic resistance thus hardly showed any advantage for improving the cell performance, caused by the densely-closed Pt sputtered layer blocking a portion of ion channels on the Nafion® surface. In order to activate the electrode/electrolyte interface at the anode, the Pt and Ru was simultaneously sputtered onto the ink-based catalyst layer in this study. The effects of the sputtered layers as well as their compositions on the cell performance were investigated by measuring the current-voltage characteristics and the cell impedance.

Experimental

Nafion® 112 (DuPont) was prepared for fabricating MEAs as the electrolyte in this experiment. Anode was made by ink-based method with Pt-Ru/C (TEC61E54, Tanaka Kikinzoku) then its surface was modified by an RF-sputtering technique: sputtering Pt-Ru catalyst onto the anode surface 30nm in thickness with different Ru/Pt compositions that controlled by the different ratios of Ru to Pt in target areas (of 0/1, 0.25/0.75 and 0.5/0.5, respectively). And, a ready-made electrode, EC-20-10 (ElectroChem, Inc.) with Pt (1.0 mg/cm^2)/C was used as the cathode. 5-cm^2 single cell testing were carried out at ambient pressure at 80°C with a 2M-CH_3OH supplied to the anode and dry O_2 fed to the cathode.

Results and Discussion

The survey scan of XPS for the sputtered electrodes with different Ru/Pt ratio is shown in Figure 1. Some strong signals of Pt (4f, 4d), C (1s) and Ru (3d, 3p) can be obviously apart from Fig. 1. The intensity of every Pt species increases with increasing the Pt loading in sputtered layer while the intensity of Ru (3d) decreases at the same time. Compared to the cases of Pt-Ru sputtered, the intensity peak of Ru (3p) has not been detected in the case of 30-nm Pt sputtered. The surface chemical composition of the Pt or Pt-Ru bimetallic layer were measured by calculating atomic ratios of Ru/Pt from the relative intensity of Pt (4f) and Ru (3d). The atomic ratios of +$Ru_{0.069}Pt_{0.931}$, +$Ru_{0.276}Pt_{0.724}$ and +$Ru_{0.546}Pt_{0.454}$ roughly agree with the expected ratios of these cases.

Figure 2 shows a comparison of the iR-free current-voltage characteristics for MEAs with and without a sputtered layer (denoted by Base-line) on the anode surface at 80°C. The performances of MEAs with a 30-nm sputtered layer exhibit better than that of the unsputtered one suggested that the sputtered Pt or Pt-Ru on the electrodes were effectively utilized for activation of the methanol oxidation. The improvements in DMFCs performance depend on the Pt loading in the sputtered layer, and the best cell performance was observed using modified anode by Pt only. Compared to the best one, the decrease in cell performance with the Ru/Pt ratio in sputtered layer from 0.25/0.75 up to 0.5/0.5 suggested that a suitable amount of Ru, which providing Pt bonded CO, should less than 0.25/0.75 in Ru/Pt atomic ratio by sputtering onto the electrode/electrolyte interface with Pt together.

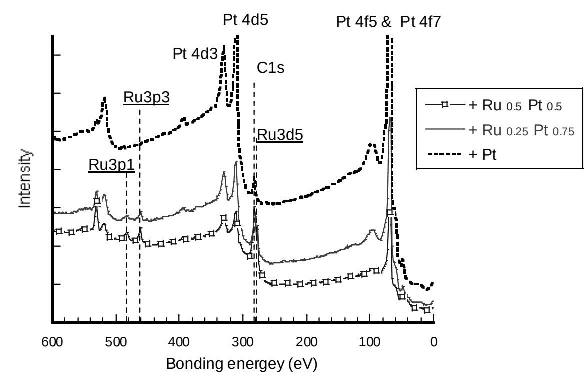

Figure 1. The survey scans of XPS for the sputtered layers (30-nm) with a different Ru/Pt ratio.

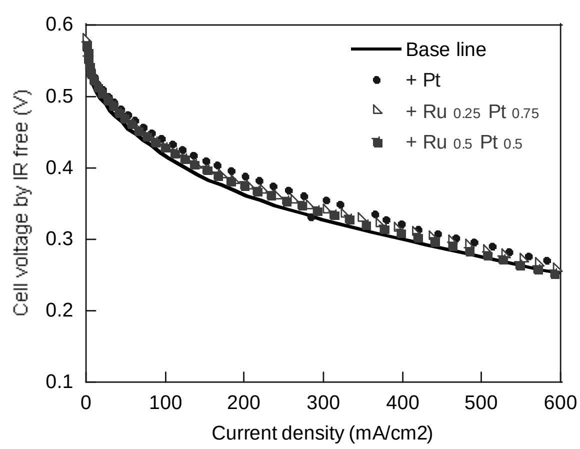

Figure 2. The performances of electrodes with and without sputtered layer at 80°C.

References

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2. Y. K. Xiu and N. Nakagawa, *J. Electrochem. Soc.,* in printing (2004).