Electro-oxidation of Methanol at Multi-walled Carbon Nanotubes Decorated with Metal Nanoparticles

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INTRODUCTION

Fuel Cells (FC) employing methanol are extremely attractive as power sources for portable applications. One of the keys to the development of FC is to find a new and improved electrocatalyst. During methanol electro-oxidation on platinum (Pt) electrocatalyst, the catalytic surface is poisoned by strongly adsorbed reaction intermediates, mainly carbon monoxide that block the active sites [1].

An approach to overcome this problem consists of alloying Pt with a second metal such as ruthenium (Ru). This allows improvement of the electrocatalytic activity of pure Pt [2]. In the present study, we report on the integration of Pt-Ru with functionalized multi-walled carbon nanotubes (MWCNT-COOH) using techniques such as high resolution scanning electron microscopy (HR-SEM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

EXPERIMENTAL

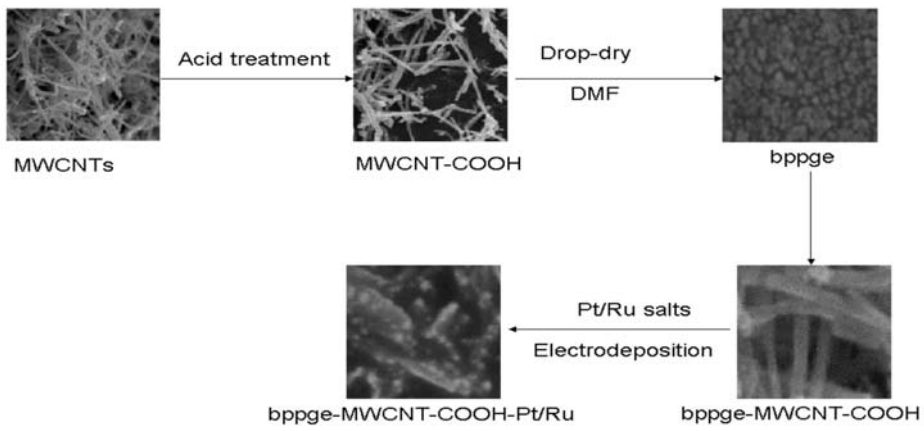

Figure 1: SEM images showing changes on the walls of MWCNTs after acid treatment and surface changes observed after basal plane pyrolytic graphite electrode (bppge) was decorated with MWCNT-COOH and electrodeposition of Pt and Ru nanoparticles using chronoamperometric technique

RESULTS AND DISCUSSION

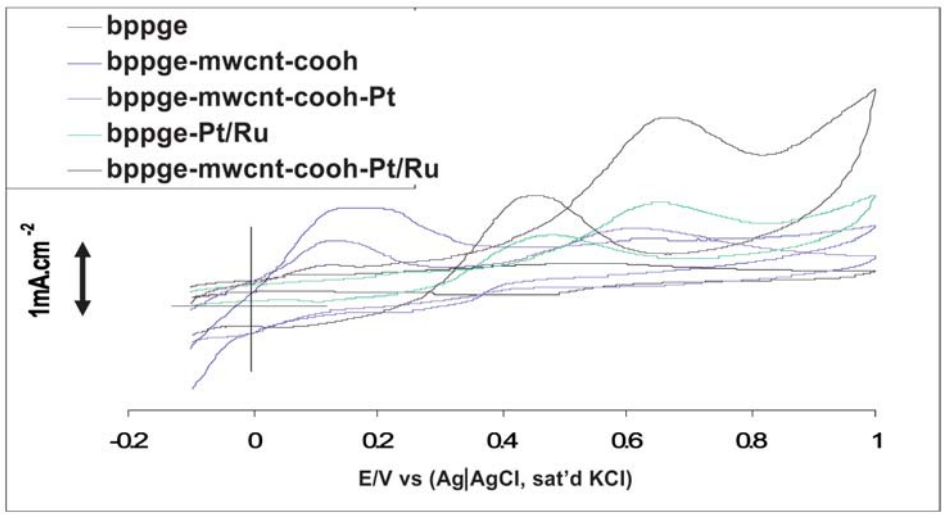

Figure 2: Comparative CV's of bare basal plane pyrolytic graphite electrode (bppge) and modified bppg electrodes in 1M CH_3OH + 0.5M H_2SO_4. This technique shows current responses of all five electrodes towards methanol (MeOH) oxidation. bppge-mwcnt-cooh-Pt/Ru displays the highest current. Scan Rate = 50mV/s

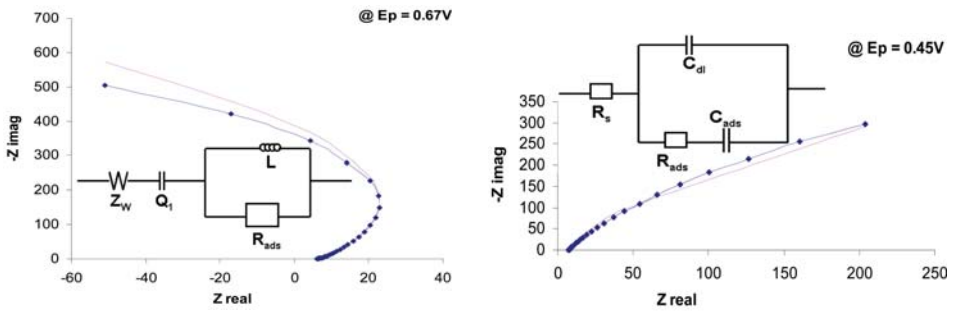

Figure 3: Nyquist plots of bppge-mwcnt-cooh-Pt/Ru for the forward and reverse peaks obtained from CV's above in 1M CH_3OH + 0.5M H_2SO_4 (dotted points represent experimental while solid lines represent fitted). Inserts are the equivalent circuits used to fit the EIS data of the electrode. Both circuits show R_{ads} indicating the adsorption process.

Using Langmuir adsorption isotherm equation (eqn 1), where β is the electrochemical adsorption equilibrium constant. The plots of $[MeOH]/Ip_{f/r}$ vs [MeOH] give straight lines

$$\frac{[MeOH]}{Ip_{f/r}} = \frac{1}{\beta Ip_{f/r}} + \frac{[MeOH]}{Ip_{f/r}} \quad (1)$$

Gibbs free energy (Δ°G) was calculated using the equation:

$$\Delta°G = - RT\ln\beta$$

High negative Δ°G obtained for the forward peak means strong adsorption

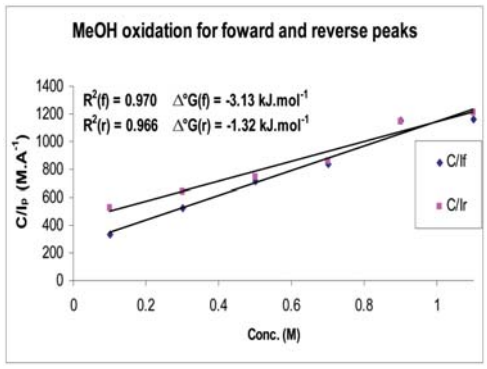

Figure 4: Plots of $[MeOH]/Ip_f$ vs [MeOH] and $[MeOH]/Ip_r$ vs [MeOH]. The concentrations of MeOH used are 0.1, 0.3, 0.5, 0.7, 0.9 and 1.1M

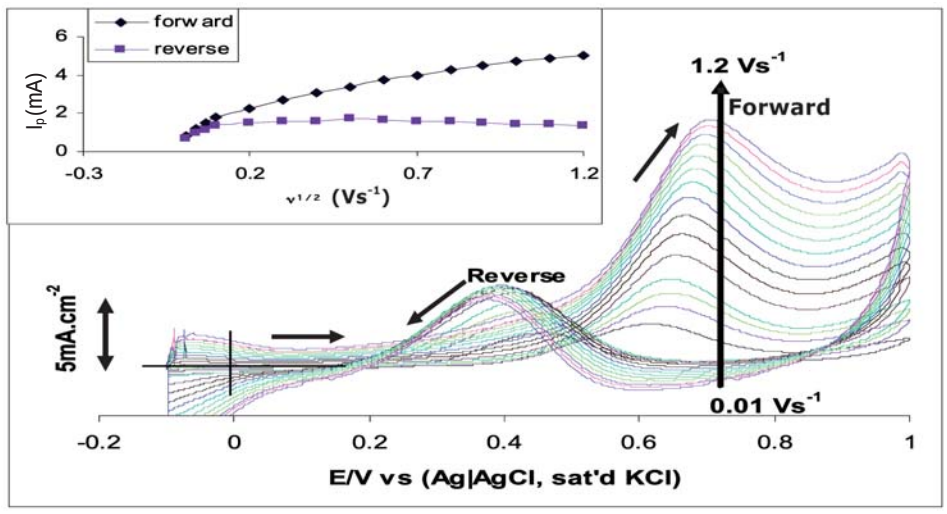

Figure 5: Scan rate studies of bppge-mwcnt-cooh-Pt/Ru. Inserts are the plots of Ip_f and Ip_r vs sqrt ν proving adsorption

$$CH_3OH + Pt \longrightarrow Pt\text{-}CO_{ads} + 4H^+ + 4e^- \quad (2)$$

$$Ru + H_2O \longrightarrow Ru\text{-}OH + H^+ + e^- \quad (3)$$

$$Pt\text{-}CO_{ads} + Ru\text{-}OH \longrightarrow Pt + Ru + CO_2 + H^+ + e^- \quad (4)$$

Figure 6: Proposed mechanism of MeOH electro-oxidation at bppge-mwcnt-cooh-Pt/Ru. During this reaction mechanism the adsorption of intermediate products can be observed at the surface of the electrode [3]

CONCLUSIONS

MWCNTs were converted to MWCNT-COOH. The presence of bright particles observed in HR-SEM image of bpgge-mwcnt-cooh-Pt/Ru confirm the successful electrodeposition of Pt and Ru nanoparticles. Electrocatalytic investigations by CV showed that bppge-mwcnt-cooh-Pt/Ru is the best electrode in terms of current response. Unlike work that has been reported on Pt/Ru nanoparticles by Z. He et al [4], our CV and EIS studies clearly prove (for the first time) that methanol oxidation at MWCNT-COOH-Pt/Ru platforms is controlled by adsorption process. This adsorption process could limit the manner in which methanol can be successfully used in fuel cells; and therefore we are currently exploring the use of alternative solvents.

ACKNOWLEDGEMENTS

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