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Spillover on a Platinum Electrode Modified by MWNTs

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Abstract: The spillover phenomenon is observed on the platinum (Pt) disk electrode modified by multi-wall carbon nanotubes (MWNTs). The rate of the spillover of oxygen-containing species produced on Pt surface to and from MWNTs is fast. However for hydrogen-adatoms, the spillover is very weak. The selective spillover on the Pt/MWNTs electrode may provide a novel way to design catalysts.

Keywords: Spillover, surface diffusion, Pt electrode, MWNTs.

The surface diffusion of reaction intermediates from the reactive sites to other inert parts is called spillover, which is an important phenomenon in catalytic chemistry. The spillover phenomenon is essential for the design of catalysts and the investigation of the reaction mechanism. It has been received much attention in the past over 10 years. However, it is difficult to distinguish the Faraday current contribution of the spillover and the interfacial reaction for a conventional electrochemical system. The reaction current enhanced by surface diffusion was first reported in 1985[1]. The spillover phenomena on various solid polymer electrolyte composite microelectrodes have recently been investigated systematically by Wu *et al*.[2-4]. In this work, we report here the first selective spillover phenomenon on a platinum electrode modified by MWNTs in aqueous solution.

A conventional three-electrode system is adopted in the experiments. A 2mm-diameter platinum disk electrode, a 0.2 mm-diameter platinum wire and a saturated Ag/AgCl electrode have been used as the work, the counter and the reference electrodes, respectively. The MWNTs is washed by acetone several times and then by distilled water ultrasonically for 30 minutes to remove the impurities. The refined MWNTs is dispersed ultrasonically in distilled water. When the Pt electrode is immersed in the MWNTs dispersed solution, the MWNTs will absorb on the Pt electrode surface physically. Thus, the Pt/MWNTs electrode is prepared. All the experiments are performed by a CHI660A system (CHI Instruments) and at room temperature ($20\pm2^{o}C$).

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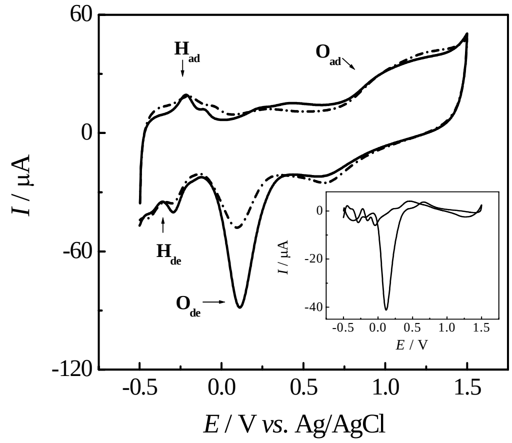
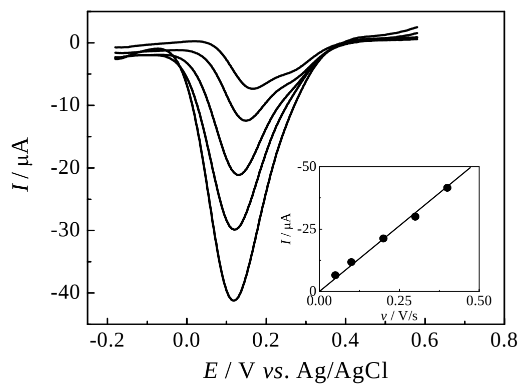
Figure 1 The voltammograms of Pt electrode without MWNTs (in dot) and with MWNTs (in solid).



The insert is the spillover enhanced current of O-containing species after background subtraction. The sweep rate is 0.4 V/s.

Figure 2 The spillover enhanced current of O-containing species at different sweep rate.



From top to bottom, the sweep rates are 0.05, 0.1, 0.2, 0.3, 0.4 V/s, respectively. The insert is linear relationship between the peak current and the sweep rate.

Figure 1 shows the votammograms of Pt electrode in 0.5 mol/L K_2SO_4 aqueous solution without MWNTs (in dot) and with MWNTs (in solid). It is obviously that the reductive current peak of the oxygen-containing species in the presence of MWNTs is much larger than that in absence of MWNTs. In the forward scan, the water will be dissociated to form oxygen-containing species such as –OH and O-adatoms on the Pt electrode surface in the positive potential region. Then the oxygen-containing species diffuse to the MWNTs surface and are stored there while the surface adsorption on Pt electrode is saturated. In the backward scan, the oxygen-containing species on the Pt electrode surface are reduced. The oxygen-containing species adsorbed on the MWNTs surface diffuse back to the surface of Pt electrode and are reduced then. This is why the reductive current peak of the oxygen-containing species is enhanced. **Figure 2** shows the relationship between the enhanced current by spillover (background subtraction from **Figure 1**) and the sweep rate. The linear relationship between the enhanced current and the scanning rate (the insert of **Figure 2**) indicates that the process is exactly a surface diffusion behavior. It is reasonable that the rate of the spillover is proportional to the sweep rate. The fast the sweep rate is, the larger the concentration grad of the oxygen-containing species at the boundary of Pt/MWNTs is, and therefore the larger spillover current is observed.

The further investigation and the mathematic model are in progress in our laboratory and will be reported elsewhere.

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