

## Effect of the surface reconstruction of Pt and its related anode catalysts on the methanol oxidation

Yimin Zhu and Carlos R. Cabrera

Department of Chemistry, University of Puerto Rico, Rio Piedras Campus, San Juan, Puerto Rico 00931-3346

Various models of the positive catalytic effects of additive elements have been proposed, such as the bi-functional model, the electronic effect and the mediating role. We noted that the methanol oxidation was promoted, in particular in the cathodic sweep, if the electrodes were prepared by sweeping between  $-0.2$  and an extended potential, such as changing the upper limit from  $0.7$  to  $1.2$  V vs. Ag/AgCl. As our knowledge, no reasonable explanation was proposed for the interesting phenomenon. A significant surface diffusion of oxides and its proton conductivity should be emphasized for the methanol oxidation.

The methanol oxidation has been investigated at Pt and Pt-Ru composite electrodes, which were electrochemically co-deposited on a glassy carbon (GC) substrate. X-ray fluorescent analysis gives the deposit bulk compositions as Pt:Ru (atomic ratio). The representative CVs for methanol oxidation at Pt are shown in Figure 1. The dash line (Pt was deposited on GC by cycling the potential between  $-0.2$  and  $1.2$  V) is somewhat different from the solid line (Pt was deposited on GC by cycling the potential between  $-0.2$  and  $0.7$  V) as two peaks of the methanol oxidation in the cathodic sweep clearly shift with the different upper limits of the preparation potential of the electrodes. The oxidation peaks are observed at ca.  $0.80$  V in the anodic sweep for both solid and dashed lines. While only an oxidation peak of methanol appears at  $0.5$  V if the cathodic sweep is extended to  $1.2$  V (dotted line).

It is reasonable that the Pt surface contains different types of oxide species, in particular, in the cathodic sweep, which may result in the different mechanisms for methanol oxidation. The peak potentials in the cathodic sweep strongly depends on the upper limit of the electrode preparation potentials, while the ones in the anodic sweep have little dependence.

In the cases of the different electrode preparation potentials, the methanol oxidation (dashed line and dotted line) in the cathodic sweep shows a higher current, compared with that of solid line. And so does it in the anodic sweep. In the same electrode preparation potentials but different upper limits of the potential sweeps, the current density in the dotted line is higher than that in the dashed line. In fact, the oxide film formed should minimize the number of active sites on the surface (in particular, due to inactive oxide formation at high potential) and hence depresses the methanol oxidation. At the same time, the CO poisoning species should also be formed in the reverse sweep, and CO is more obvious below about  $0.6$  V (below its oxidation potential), however, we can observe big current for the methanol oxidation still, in particular at ca.  $0.5$  V. The pretreatment at the controlled upper limit of  $1.2$  V may produce phase oxide (not only surface oxide), which affects the methanol oxidation and changes the electronic properties and proton conductivity of electrodes. This is easier to understand than a surface area increase or an active-site effect. The phase oxide layer may be formed at higher potential through the surface diffusion. The porous micro-structure with proton conductivity in the phase oxide layer may be induced by the more reconstructed Pt oxide layer

beyond  $1.0$  V based on the limited oxide diffusion promoting the reconstruction since the reduction will occur after only limited surface diffusion. This favors for the methanol oxidation with proton transfer by increasing the catalytic site-efficiency.

Figure 2 shows the CV of the Pt electrode in  $0.05$  M  $\text{KBrO}_3$  and  $0.1$  M  $\text{H}_2\text{SO}_4$ . The catalytic reduction of bromate is observed below  $0.2$  V. The well-defined redox peaks at  $0.9$  and  $1.0$  V is very interesting because the formation or reduction of Pt oxides may not produce so reversible peaks and because the redox of bromate may also not produce such peaks. The reversible feature at ca.  $1.0$  V in CV may be due to a reversible reconstruction of the oxidized surface (i.e., the oxidized surface is reconstructed and the reconstruction is removed by reduction), rather than to an OH adsorption process at this potential (which can be confirmed by inhibition of the methanol oxidation). Bromate is very helpful to probe this reversible feature, possibly due to further limit of surface diffusion by interaction between bromate and the oxidized surface (possibly involving the formation of a bromate-hydrogen containing oxide complex). In general, the formation of hydrogen-containing oxide is more pronounced for hydrated oxide layers in which the insertion of a proton is thermodynamically more favorable than the rupture of Pt-O bonds. Thus, bromate incorporated surface diffusion is a possible explanation for the reversible behavior at ca.  $1.0$  V, in which the insertion of a proton reflects the proton conductivity of the oxidized surface.

Similar enhanced methanol oxidation, in particular, in the cathodic sweep was also observed at Pt-Ru. XPS results confirm the presence of Ru on the Pt-Ru surface. Ru electrode also shows a reversible redox behavior at ca.  $1.0$  V in  $\text{KBrO}_3$ .

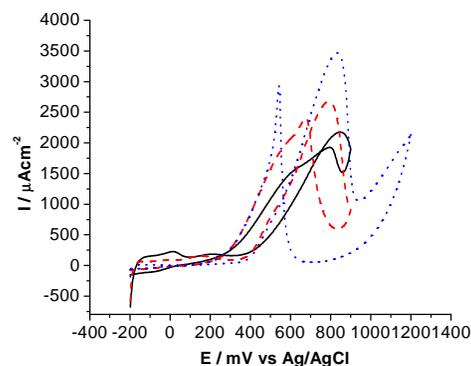


Fig 1 CVs for the methanol oxidation in  $1$  M  $\text{CH}_3\text{OH}/0.1$  M  $\text{H}_2\text{SO}_4$  at  $50$  mV/s, (—) at Pt, prepared by cycling potential between  $-0.2$  and  $0.7$  V; (---) and (···) at Pt, the upper limit of preparation potentials is extended to  $1.2$  V.

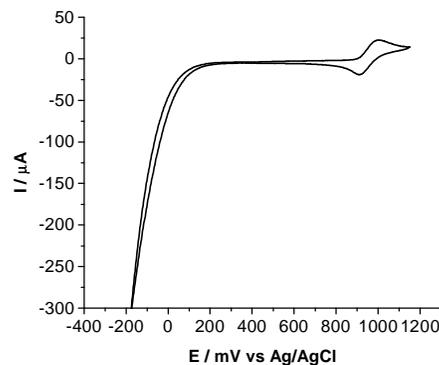


Fig 2 CV of  $0.05$  M  $\text{KBrO}_3$  and  $0.1$  M  $\text{H}_2\text{SO}_4$  at  $50$  mV/s at Pt, prepared by cycling potential between  $-0.2$ ~ $1.2$  V.