

Letters to the Editor

Enhanced methanol electrooxidation activity of PtRu nanoparticles supported on H₂O₂-functionalized carbon black

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PtRu nanoparticles deposited on a carbon black substrate are catalysts commonly employed for the electrooxidation of methanol and carbon monoxide-containing hydrogen feeds [1,2]. However, improvement of effective electrocatalysts is an essential goal in the development of a practical DMFC. The use of carbon black as a support for noble metals is frequent in the electrodes of polymer membrane electrolyte fuel cells, but the impact of the chemical and physical properties of the carbon on electrocatalytic performance are not yet sufficiently understood. The presence of oxygen surface groups influences the surface behaviour of carbons to a considerable extent [3,4]. As examples, the wettability and adsorptive behaviour of a carbon, as well as its catalytic and electrical properties, are influenced by the nature and extent of such surface groups. The varying role of oxygenated functionalities on the formation of the dispersed platinum has been established [5–8], but not with an additional metal such as ruthenium. In the present investigation we report how the performance in methanol electrooxidation of PtRu nanoparticles deposited on a carbon black substrate, previously functionalized with oxygen surface groups, is improved.

A commercial Vulcan XC-72R (Cabot Co.) carbon black was used as the support material. This carbon was functionalized by treatment with an aqueous H₂O₂ solution (10 v/v%) at room temperature for 48 h under stirring. Then, the solid was dried at 120 °C for 24 h. This sample was labelled as Vulcan-O. PtRu electrocatalysts were prepared by colloidal methods [9]. This method is based on the co-deposition of fine oxides of platinum and ruthenium at an atomic scale, from a mixed salt solution of the metals in presence of NaHSO₃, followed by reduction with hydrogen bubbling. Catalysts were labelled as CPR (30 wt% PtRu(1:0.7)/Vulcan XC-72R) and CPRO (30 wt% PtRu(1:0.7)/Vulcan-O). Commercially available catalyst 30 wt% PtRu(1:1)/Carbon (HiSPEC 5000, Johnson & Matthey) was used for comparison. Commercial catalyst is in powder form and its crystallite size determined by XRD is 2.2 nm.

Determination of the nature of the oxygen surface groups in the carbons was accomplished by temperature-programmed evolved gas analysis with mass spectroscopy (EGA-MS) under Ar. Fig. 1 depicts both the CO and CO₂ desorption profiles of the supports. It may be observed that H₂O₂ treatment generated an intense oxidation that resulted in large CO₂ and CO evolutions between 100–600 °C and 400–900 °C, respectively, compared with the untreated carbon Vulcan XC-72R. Surface oxygen groups decomposed upon

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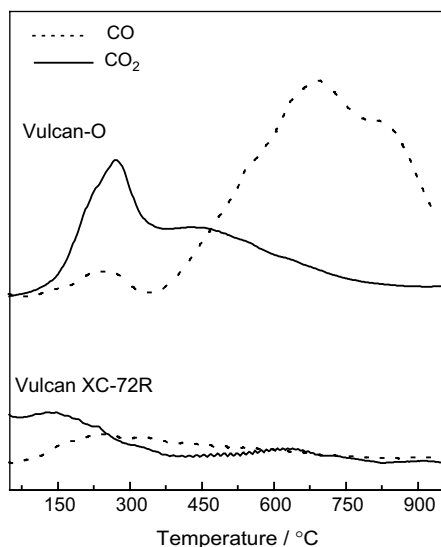


Fig. 1. EGA-MS of Vulcan XC-72R and Vulcan-O.

heating under the inert atmosphere; the most acidic groups (carboxylic groups and their derivatives, such as lactones and anhydrides) evolved CO_2 , and the least acidic groups (quinones, hydroquinones, ethers, carbonyls and phenols) evolved CO [10,11]. These results indicate that treatment with H_2O_2 develops both types of acid group, and most of these groups are weak acid groups that decompose at higher temperatures than the strong acid ones.

Particle size and PtRu dispersion were evaluated from the transmission electron microscopy (TEM). The particle size distribution of both catalysts CPR and CPRO was found to lie between 2 and 2.5 nm by TEM. Fig. 2 shows the particle size distribution of the CPRO catalyst. Apparently, oxidation of the support did not lead to changes in the PtRu particle size. However, agglomeration of small PtRu nanoparticles was found to occur on the CPRO electrocatalyst.

Surface characterization of CPR and CPRO catalysts was analyzed by XPS. Spectra of $\text{Pt}4f_{7/2}$ and $\text{Ru}3p_{3/2}$ levels of both catalysts show components corresponding to metallic Pt and Ru with different electronic effect (71.6–71.9 eV for $\text{Pt}4f_{7/2}$ and 462.3–463.1 for $\text{Ru}3p_{3/2}$), and to Pt^{2+} species (72.9–73.3 eV). However, only CPR catalyst show a further component at higher BE (74.7 eV for $\text{Pt}4f_{7/2}$ and 465.1 eV for $\text{Ru}3p_{3/2}$) corresponding to a higher oxidation state (Pt^{4+} and Ru^{4+}), which is not present in the CPRO catalysts. Moreover, O1s spectra (Fig. 3) show, beside the signals corresponding to $\text{C}=\text{O}$ (531.2–531.4 eV) and $\text{C}-\text{O}$ (533.1 eV) groups, a component at 530.46 eV in the CPR catalyst, which can be taken as being conclusive of the presence of MeO (Me = Pt, Ru) [12]. This last component is not present in CPRO catalyst. From these data, it is clear that platinum and ruthenium are less oxidized on Vul-

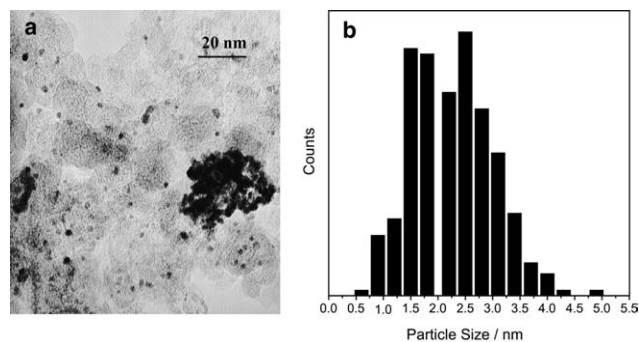


Fig. 2. (a) TEM photograph and (b) particle size distribution of CPRO catalyst.

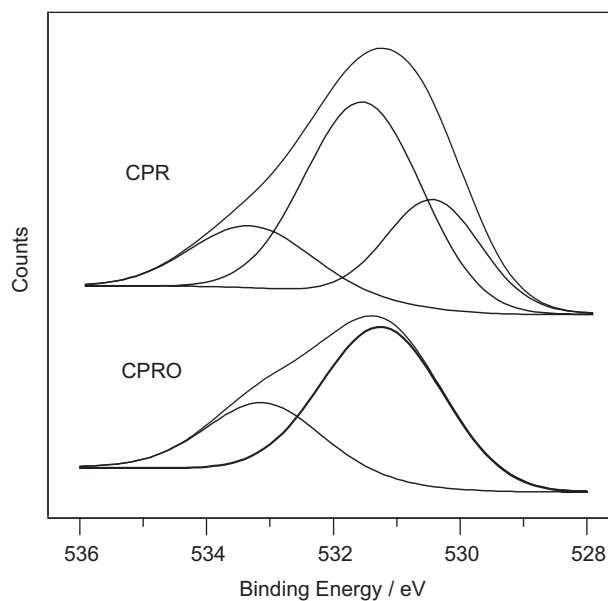


Fig. 3. XPS spectra of O1s of CPR and CPRO catalysts.

can-O than over the Vulcan XC-72R support, indicating that both metals have a high oxidation-resistance over this oxidized support [13]. Quantitative evaluation of PtRu content by XPS revealed that the concentration of the metals in the external exposed surface was much lower on CPRO (7% wt) than on the CPR (21% wt) counterpart.

Electrochemical measurements were carried out in a standard three electrodes electrochemical cell. The working electrode was prepared according to a modified method developed by Schmidt et al. [14]. All potentials were referenced to the reversible hydrogen scale (RHE). Prior to the CH_3OH oxidation studies, the catalysts were characterized by CO_{ads} stripping voltammetry. The stripping technique provides information about the facility of the material towards CO oxidation, which can be directly correlated with the nature of the material, and the extent of the CO oxidation process gives information about the amount the activity area of the

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