Measurement of the activity of small clusters of fuel cell electrocatalysts using nm sized carbon electrodes

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Within the literature there has come to be accepted that compared to bulk electrodes, highly dispersed platinum can provide higher specific activity and is less strongly poisoned by reaction intermediates [1]. The size effect of platinum [2,3] and platinum-ruthenium particles [4] for the methanol electro-oxidation is well established. An optimum diameter of the catalyst particles was suggested as about 2~3 nm. Moreover, fine control of the interparticle distance is suggested as being a necessary prerequisite for efficient catalysis[5].

Although much work has been performed using platinum microelectrodes to examine mass transport effects at small electrodes, most work on highly dispersed platinum electrocatalysts involves the fabrication of large macroscopic electrodes. We have pioneered the development of carbon microelectrodes with effective radii down to one nm [6]. These electrodes are produced using a multistep process as shown in fig 1, and are typically characterised using oxidation or reduction of a reversible redox couple, fig 2.

In this paper we use these carbon microelectrodes as substrates for the deposition of small platinum particles using both chemical and electrochemical deposition techniques – thus the carbon electrode acts in exactly the same way as carbon particles do during the formation of supported fuel cell electrocatalysts. Our approach allows us to study the effect of electrocatalyst particle size on activity under well-defined mass transport conditions and provides a route to determine the intrinsic activity of individual catalyst particles.

Displayed in fig. 2(a) is the cyclic voltammogram of a platinum particle electrodeposited on a carbon nano electrode. Fig. 2(b) shows the voltammetric response in the presence of hexacyanoferrate (III) and dissolved dioxygen. Fig. 3 shows the effective number of electrons transferred as a function of platinum particle diameter. The values were calculated from the diffusion limited currents, saturated concentration of oxygen and platinum particle size as determined from the hexacyanoferrate (III) reduction current. The effective electron transport number decreases as a function of electrode size. This effect occurs because of the enhanced transport of the peroxide intermediates away from the electrode at smaller electrode sizes.

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References

[1]N. T. Napporn, L. Laborde, J. M. Leger, C. Lamy, J. Electroanal. Chem. 404 (1996) 153.

[2] Y. Takasu, T. Iwazaki, W. Sugimoto, Y. Murakami, Electrochem. Comm. 2 (2000) 671

[3] T. Frelink, W. Visscher, J. A. R. Veen, J. Electroanal. Chem. 382 (1995) 65.

[4] Y. Takasu, H. Itaya, T. Iwazaki, R. Miyoshi, T. Ohnuma, W. Sugimoto, Y. Murakami, Chem. Commun. 2001, 341.

[5] M. Watanabe, S. Saegusa, P. Stonehart, J. Electroanal. Chem. 271 (1989) 213

[6] S. Chen, A. Kucernak, Electrochem. Comm, *In Press.*

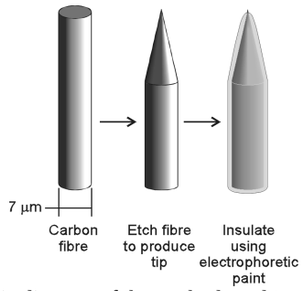

Fig. 1 Schematic diagram of the method used to produce ultrasmall carbon electrodes.

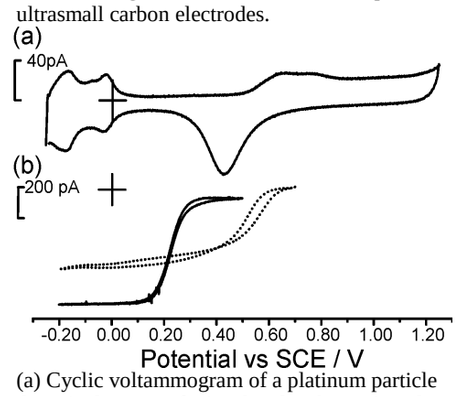

Fig. 2 (a) Cyclic voltammogram of a platinum particle deposited on top of a insulated carbon microelectrode in 0.5 mol dm^{-3} H_2SO_4.$r_{eff,carbom}$=500 nm; $r_{eff,Pt}$=3.6 μm. (b) Voltammogram of above electrode in 0.01 mol dm^{-3} $K_3Fe(CN)_6$, (—); Saturated oxygen (·····). ν=25 mV s^{-1}

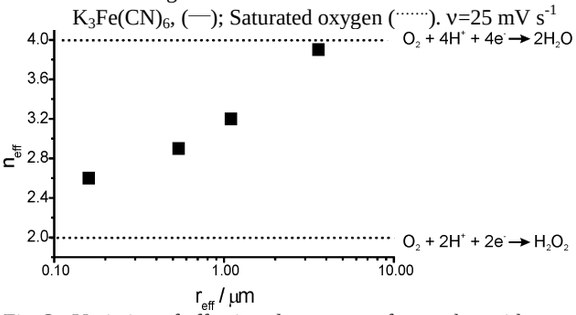

Fig. 3 Variation of effective electron transfer number with radius of the platinum particle deposited on a carbon nano electrode.