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Enhanced durability of a Pt/C electrocatalyst derived from Nafion-stabilised colloidal platinum nanoparticles

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ABSTRACT

A Pt/C electrocatalyst was prepared from colloidal Pt nanoparticles stabilised by Nafion. This electrocatalyst was found to exhibit negligible degradation under a potential cycling regime conducted on a model thin-film catalyst layer in a 3-electrode cell set-up, in which an *E-Tek* Pt/C commercial catalyst showed a 23% loss of specific electrochemical surface area (*SECSA*). The enhanced durability of the Nafion-derived is thought to arise from the protection of Pt particles against dissolution and sintering by the surrounding Nafion layer. The use of the ionomer phase as a protective agent in the catalyst layer presents a novel strategy for the production of more durable Pt/C catalysts for the Proton Exchange Membrane Fuel Cell (PEMFC), which currently presents a significant challenge for the commercialisation of this technology.

1. Introduction

Cost and durability remain significant technological barriers to deployment of PEMFC systems for the automotive and domestic sectors [1]. This is due to the fact that the catalyst layers (CLs) within PEMFC electrodes contain Pt-based electrocatalysts which are costly and prone to degradation under extended operating conditions [2]. Optimisation of the composition and morphology of the CL (5-20 μm) to maximise Pt utilisation (at low Pt loadings) and minimise degradation can therefore make a significant contribution towards reducing the overall cost and improving the long-term durability of PEMFC stacks.

The CLs are complex heterogeneous structures containing an ionomer (Nafion®) for ionic (H^+) conduction and a carbon black for electronic conduction, with sufficient porosity for transport of reactant gases and removal of waste water. The hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) at the anode and cathode respectively, occur at the triple-phase boundary between ionomer, carbon support and catalytically active Pt surface sites [2]. The triple-phase boundary is commonly extended throughout the CL by adding a dispersion of Nafion® ionomer to the ink containing the supported catalyst [3].

Whilst subject to ongoing debate, it is generally accepted that degradation of PEMFC Pt-based electrocatalysts proceeds via three main mechanisms: (i) dissolution of Pt, leading to Pt mass loss and particle growth via Ostwald ripening upon redeposition [4]; (ii) agglomeration and sintering of Pt particles via diffusion on the carbon support [5]; (iii) corrosion of the carbon support [6]. The net effect of these processes is to decrease the specific electrochemically-active surface area (*SECSA*), resulting in reduced PEMFC power density.

It is proposed that dissolution and sintering processes could be inhibited by employing capping surfactants, as is commonplace in the synthesis of colloidal nanoparticles [2] to control growth and prevent agglomeration via steric and electrostatic stabilisation mechanisms. Such stabilisers are usually inert and must normally be removed to obtain good performance in catalysis applications [7,8]. Ordinarily this presents an additional complication when deriving electrocatalysts from colloidal nanoparticles, but if Nafion® is used a stabiliser then this step becomes unnecessary – even undesirable – as Nafion® forms an active component of the catalyst layer.

In this work, we report a highly durable Pt/C electrocatalyst derived from Nafion®-stabilised colloidal Pt nanoparticles. This novel catalyst preparation route presents a new strategy for improving the durability of PEMFC electrodes by employing the ionomer phase as a protective agent for Pt nanoparticles within the CL.

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2. Experimental

Nafion®-stabilised colloidal Pt was prepared by chemical reduction of an aqueous $PtCl_6^{2-}$ precursor in the presence of Nafion®. Nafion® dispersion (10 wt.% in water, EW 1100, Fuel Cell Store) was added to a 5 ml aliquot of 2.21 mM $H_2PtCl_6.6H_2O$ (>99.9% Sigma) solution to achieve a Pt:Nafion mass ratio of 1:30. After stirring at 600 rpm for 30 mins, a 500 µl aliquot of 87 mM $NaBH_4$ (ACS Reagent, Sigma) solution was then infused through a stainless steel needle at 48.5 ml.min^{-1} using a syringe pump. Excess Nafion® was removed from the product by 1:1 v/v dilution with acetone, followed by centrifugation and ultrasonic redispersion in a 1:4 v/v water/acetone mixture up to 3 times. Nafion® content of the purified colloidal Pt was determined by TGA. A carbon black (Vulcan XC-72R, Cabot Corp.) was then added to the purified colloidal Pt under sonication in the ratio of 1:4 of Pt:C (m/m).

The Nafion®-derived Pt/C was compared against a catalyst ink prepared using a standard method by mixing *E-Tek* 20 wt.% Pt/C commercial catalyst with a quantity of Nafion® dispersion required to form the optimal 33 wt.% Nafion® concentration in the dry catalyst layer reported previously [9,10]. The water/acetone ratio in the standard ink was also maintained the same as in that of the Nafion®-derived catalyst.

For electrochemical characterisation, working electrodes were prepared by pipetting a 5-7 µl aliquot of Pt/C catalyst dispersion onto a 3 mm glassy carbon disc electrode (GC, Radiometer Analytical) to achieve a Pt loading of 40 µg cm^{-2}. After drying in a vacuum oven, a ~100 nm thick Nafion® film was cast over the catalyst by pipetting 5 µl of a Nafion® solution [11], suitably diluted using Eq. (1):

$$[\mathit{Nafion}^{\circledR}] = \pi r^2 \tau \rho_{Nafion} v^{-1} \tag{1}$$

where *[Nafion®]* is the Nafion® concentration in mg ml^{-1} required to form a film of thickness τ (µm) on an electrode of radius r (mm) on deposition of a droplet of volume v (µl), and assuming a dry Nafion® film density of $\rho_{Nafion} = 1.98$ g cm^{-3} [12].

All electrochemical experiments were performed at 298 K in a 3-electrode cell, using an Autolab PGSTAT302N potentiostat (Eco-Chemie) and a rotating disc electrode (RDE) setup (ED101, Radiometer Analytical). The background electrolyte was 0.1 M $HClO_4$, prepared from 70% (AR, Fisher), purged with N_2 gas for at least 20 minutes. Potentials are reported against the normal hydrogen electrode (NHE). Ultra-pure water (18.2 MΩ, Millipore) was used throughout.

Cyclic voltammetry (CV) was conducted between 0.05 V and 1.2 V at 250 mV s^{-1} (30 scans). *SECSA* in m^2 Pt g^{-1} was measured from voltammetric profiles recorded at 25 mV s^{-1} by integrating in the hydrogen underpotential deposition (H_{upd}) region (0.0-0.4 V) using Eq. (2) [2]:

$$SECSA = \frac{Q_{Hdes}.100}{210.L_{Pt}.A} \tag{2}$$

where Q_{Hdes} (µC) is the charge measured upon desorption of a monolayer of underpotentially-deposited (UPD) hydrogen, L_{Pt} is the Pt loading (µg cm^{-2}), A is the geometric area of the GC (cm^2) and the value 210 µC cm^{-2} corresponds to the charge passed during hydrogen UPD on a bulk polycrystalline Pt surface.

Accelerated catalyst degradation was induced by performing linear sweep voltammetry (LSV) between 0.05 V and 1.2 V at 25 mV s^{-1}, with 50 sweeps in each of N_2- and O_2-purged electrolytes by RDE at various rotation speeds (400-3000 rpm), allowing an equilibration period of 5 s at 0.05 V between each sweep. Following the degradation cycle, *SECSA* was re-measured as above. Detachment of the catalyst during rotation was ruled out by comparing Pt content across several areas of the GC before and after electrochemical testing, using energy dispersive x-ray spectroscopy (EDS, Oxford ISIS) in a scanning electron microscope (SEM, JEOL 6060, 20 kV). Size distributions for Pt nanoparticles on catalyst pre- and post-electrochemical cycling were obtained from transmission electron microscope (TEM, JEOL 1200ex, 80 kV) images by measuring at least 150 particles using ImageJ software.

3. Results and Discussion

Fig. 1(a) and (b) show TEM micrographs of the Nafion-derived and commercial catalysts. In the Nafion®-derived catalyst, Pt nanoparticles appear to form loosely-agglomerated networks on the carbon support, which could indicate coordination with Nafion® ionomer chains. In comparison, Pt nanoparticles in the *E-Tek* catalyst are well-dispersed over the carbon support [Fig. 1(b)]. Size distributions in Fig. 1(c) and (d) reveal that the Pt nanoparticles in the Nafion®-derived catalyst are in average larger (~7 nm) and more polydispersed than those on the *E-Tek* catalyst (2-3 nm). The physical surface area of the Nafion®-derived and commercial catalysts were calculated as 36 m^2 Pt g^{-1} and 90 m^2 Pt g^{-1} respectively using a spherical approximation. The value for the *E-Tek* catalyst is in excellent agreement with previous reports [13,14].

For the Nafion®-derived catalyst, the *SECSA* measured was found to be 34 ± 1 m^2 Pt g^{-1}, corresponding to around 93% utilisation of Pt surface area. This compares favourably against the *E-Tek* catalyst, which attains a catalyst utilisation of only 50%, although in absolute terms it still displays a superior *SECSA* of 45 ± 4 m^2 Pt g^{-1} owing to its smaller Pt particle size. Several studies have shown that in a standard CL preparation, the added Nafion cannot penetrate into micropores (<2 nm-Ø) within the carbon support [15]. This implies that Pt nanoparticles residing within carbon micropores are isolated from the proton-conducting network, and are consequently unutilised. It should be noted that whilst the *E-Tek* catalyst was prepared at the optimal Nafion® content of 33 wt.%, the Nafion® content of the Nafion®-derived Pt/C was unoptimised – being determined entirely by the amount that happened to be removed by 3 centrifugation steps (11.5 wt. %). It may be possible to attain 100% utilisation by optimising the Nafion® content.

Comparison of cyclic voltammograms in Fig. 1 c & d reveals that both catalysts display a reduction in the charge due to oxide formation/reduction in the potential region between 0.6-1.2 V, which may be attributed to Pt surface reconstruction as a result of place-exchange during repeated oxide formation/reduction cycles [16].

After electrochemical cycling, the Nafion®-derived catalyst showed negligible loss of *SECSA* based on H_{upd} charge and no evident changes in particle size [Fig. 1(c)]. Meanwhile, the *E-Tek* catalyst suffered a ~23% loss of *SECSA* and showed a distinct growth in Pt nanoparticle size [Fig. 1(d)] which resulted in a ~28% loss in physical surface area. EDS data indicated that the Pt loading was unaffected by electrochemical testing. The close correlation between loss of *SECSA* and physical surface area provides strong evidence that particle growth is the main degradation mechanism under this cycling regime. The results of electrochemical cycling for both catalysts are summarised in Fig. 2.

Although the Pt nanoparticle size of the Nafion®-derived catalyst is larger than that of the *E-Tek,* it is unlikely that this has a significant effect on the dissolution rate since the dissolution potential of Pt deviates significantly from the bulk value only as particle size decreases below 1 nm [17]. Size-dependent differential particle growth has been observed previously for Pt/C catalysts [18], but given the extent of the particle growth observed here for the E-Tek Pt/C, it is likely that some measurable growth would have been observed for the Nafion-derived catalyst if growth mechanisms were in effect. The absence of measurable particle growth implies that one or more