Nanoparticulate platinum films on gold using dendrimer-based wet chemical method

S RAGHU, SHEELA BERCHMANS, K L N PHANI and V YEGNARAMAN
Central Electrochemical Research Institute, Karaikudi 630 006, India
E-mail: kanalaphani@yahoo.com

Abstract. There is a growing interest in devising wet chemical alternatives for physical deposition methods for applications involving thin films, e.g., catalysis. Deposition of platinum on thin gold films is often a problem leading to incomplete coverage and improper adhesion to solid surfaces. Gold substrates often need pre-activation for achieving complete coverage. We demonstrate here that dendrimers with proper functionalities and size work as well-defined nucleating agents and adhesion promoters. This feature is demonstrated using an amine-terminated dendrimer of generation 4.0. This approach allows one to obtain adherent nanoparticulate films of platinum on gold. Unlike other nucleating agents and adhesion promoting compounds, dendrimers have a well-defined ordered structure in terms of their space filling ability.

The stability of the films obtained with adsorbed dendrimers is demonstrated using the electrocatalytic reactions of fuels like methanol. The films formed without dendrimers cannot sustain the electro-oxidation currents due to the instability of the films while the films formed with dendrimers can sustain currents for longer duration and for several cycles. The dendrimer-derived Pt films exhibit higher catalytic activity compared to other methods.

Keywords. Nanoparticulate films; platinum; electrocatalysis; adhesion promoters; PAMAM dendrimers.

PACS Nos 82.45.Fk; 82.45.Mp; 82.35.Np; 68.37.Ps

1. Introduction

Highly dispersed high surface area catalysts are used in many catalytic and electrocatalytic processes and are very important for heterogeneous catalysis and fuel cell applications. In majority of fuel cells, the catalysts used are platinum and platinum alloy colloidal particles that are either supported or unsupported [1–3]. Various support materials have been explored for the preparation of platinum-based catalysts [4–6]. Recently, there has been growing interest in devising wet chemical alternatives for physical deposition methods for applications involving thin films. Deposition of platinum on thin gold films is often a challenging problem leading to incomplete coverage and improper adhesion. Such films often pose problems in obtaining sustained current in devices such as fuel cell membrane–electrode assemblies due to *peeling-off* of the catalyst films. In this work, we have explored the use of dendrimer molecules to form micro- and nanoparticulate platinum films on gold substrates.

Dendrimer molecules represent an important building block for a wide variety of technological applications. Their architecture allows for unprecedented control of a macromolecular framework as a function of size, shape, flexibility and surface chemistry within the nanoscale regime.

The dendrimeric framework has previously produced composite materials based on its use as a porogen in sol–gel networks [7]. Selection of a specific generation of dendritic template dictates the overall size dimension of the pore after calcination of the composite materials. Previous work also has shown that PAMAM and PPI dendrimers represent biomimetic analogs of the mesoporous silica precipitating polyamine isolated from diatoms [8,9]. Dendrimers are also excellent hosts for a diverse array of nanoparticles [10–15]. In contrast to traditional polymers, dendrimers are unique core–shell structures possessing three basic architectural components (figure 1): a core, an interior shell (generation) consisting of repeating branching units and terminal functional groups (the outer shell or periphery) that can serve as anchors or 'handles' to link them to the electrode surfaces. The structure of a PAMAM dendrimer molecule has a central core which can be ammonia, ethylenediamine or cystamine. The repeating branching structures contain amide bonds that can chelate metal ions and the outer periphery may contain amine, carboxylate or hydroxyl functionalities. In this work, we have employed the self-assembly of amine-terminated fourth generation PAMAM dendrimers to form a base layer over which a thin film of Pt is formed by chemical reduction using a mild reducing agent, hydroxylamine hydrochloride. The external amine groups

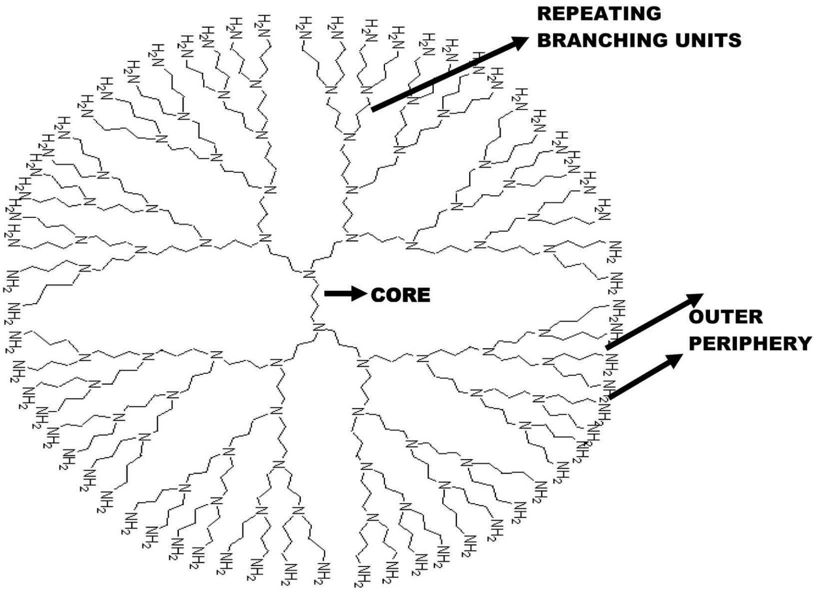

Figure 1. Structure of a fourth generation amine-terminated PAMAM dendrimer G_4NH_2.

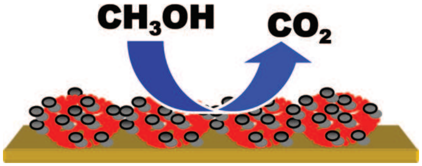

Figure 2. Scheme representing methanol oxidation on nanoparticulate Pt film on gold surface.

chelated to platinum ions serve as nucleating agents for the growth of a thin film of Pt (figure 2). The formation and characterization of such thin films and their electrocatalytic behaviour towards the oxidation of small molecules like methanol are also discussed in this paper.

2. Experimental

Fourth-generation amine-terminated PAMAM dendrimer, G_4NH_2 supplied by Aldrich and the reducing agent, hydroxylamine hydrochloride (Ranbaxy) were used *as received.*

Gold substrates (1000 Å gold coating on silicon wafers with an intermediate adhesion layer of Ti, 100 Å thickness procured from Lance Goddard Associates, USA) of geometric area of 0.5 cm^2 were used for platinum film formation and working electrodes for electro-oxidation of methanol.

Formation of Pt thin films on gold substrates

Gold substrates were cleaned by sonication in distilled water for 5 min and then immersed in a solution of NH_2-terminated PAMAM dendrimer (0.035 mM) in ethanol overnight. After 24 h, the substrates were removed and subjected to refluxing in the presence of hydroxylamine hydrochloride (1%) and 10 mM K_2PtCl_4 for 5 h at 60°C. The stability of the dendrimer-derived films was checked in the electrochemical cell containing the supporting electrolyte. The films deposited without the dendrimer, while being patchy, were found unstable in the electrolyte solutions.

Electrochemical characterization

Cyclic voltammograms were recorded using a Wenking Potentioscan (POS 88) along with an x-y/t recorder (Rikadenki, Japan). Pt electrode was used as a counterelectrode and a $Hg/Hg_2SO_4/0.5$ M H_2SO_4 (MSE) was used as the reference electrode. The experiments were carried out in 0.5 M H_2SO_4 solutions.

Impedance spectra were recorded in a frequency range of 10 mHz to 100 kHz in 0.5 M H_2SO_4 with the Pt film electrode at potentials 0.3 V and 0.11 V (the potentials corresponding to the oxidation of methanol in the forward and reverse scans respectively).

Scanning electron microscopic images were recorded for the samples with a magnification of around ×100. Atomic force microscopic images were recorded with a molecular imaging PicoSPM using gold-coated silicon nitride of 30 nm cantilevers (force constant of 0.12 N/m).

3. Results and discussion

Figure 3 represents the SEM image of the Pt thin film formed on the gold substrate. The image shows an even distribution of Pt particles on the gold substrate. The size of the particles ranges between 200 and 300 nm. Figure 4 shows the AFM image of the Pt films formed on the gold substrate. The AFM image represents

Figure 3. SEM image of Pt film formed on the gold substrate at a magnification of ×100.

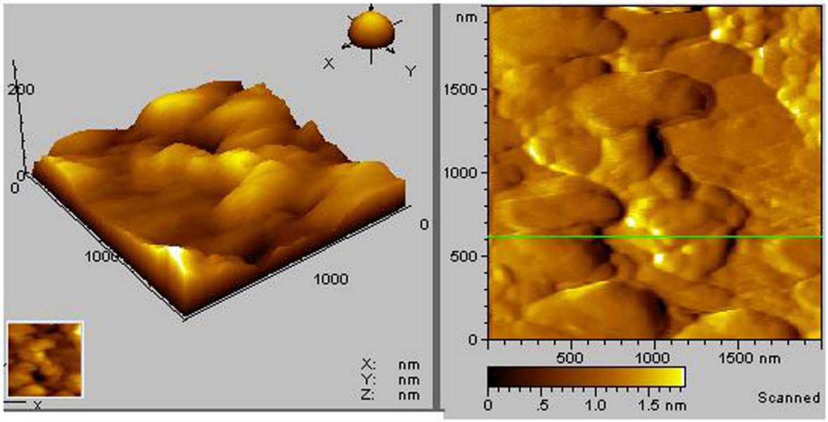

Figure 4. AFM images of Pt film on the gold substrates.

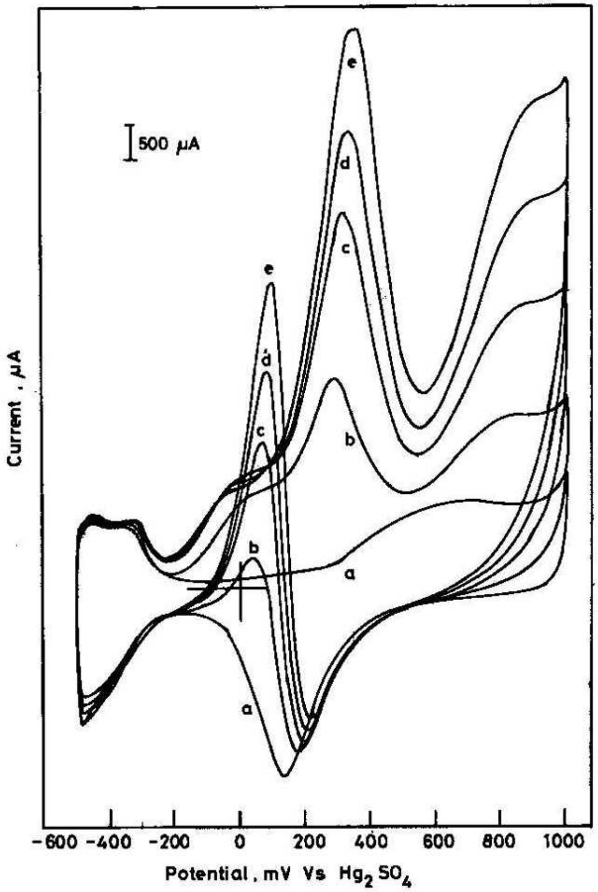

Figure 5. Cyclic voltammogram representing methanol oxidation with the potential scan range −0.6 V to 1.0 V at a scan rate of 50 mV/s for different methanol concentrations: (**a**) 0 M, (**b**) 0.017 M, (**c**) 0.034 M, (**d**) 0.051 M and (**e**) 0.068 M.

the magnified version of the SEM image and the distribution of uniformly sized Pt particles on the substrate is clearly seen in the AFM image.

The cyclic voltammograms representing the methanol oxidation in the potential range −0.6–1.0 V are shown in figure 5. The onset of electro-oxidation occurs at a very low potential of −0.25 V and the peak potential also occurs at a low overpotential of 0.31 V. The current density corresponding to the oxidation of methanol (0.017 M) is found to be 1600 $\mu A/cm^2$ and is quite high compared to many systems reported in literature [16]. The oxide peak appearing after the peak corresponding to the catalysis of methanol oxidation also increases with the addition of methanol. This is attributed to the oxide-assisted catalysis of methanol.

Figure 6 presents the cyclic voltammogram for methanol oxidation in the restricted potential range of −0.6 V to 0.4 V. The methanol oxidation peak in the

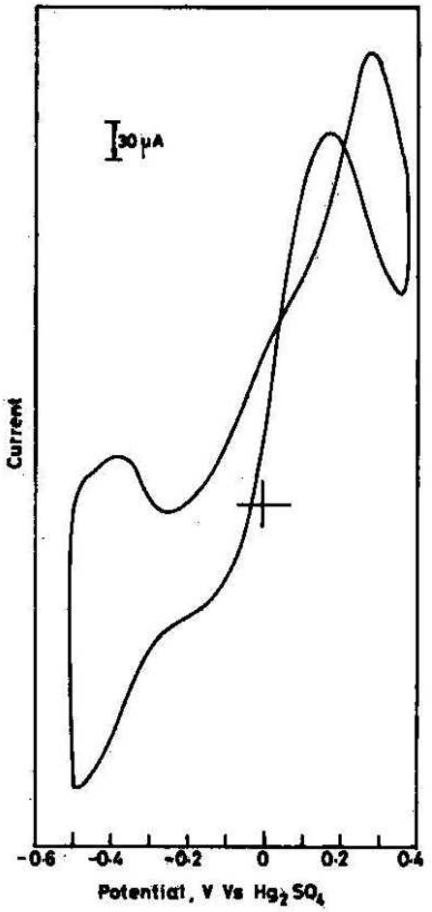

Figure 6. Cyclic voltammogram representing methanol oxidation with the restricted potential scan range −0.5 V to 0.4 V at a scan rate of 50 mV/s for a methanol concentration of 0.068 M.

forward scan as well as the methanol oxidation peak in the reverse scan are clearly seen in this voltammogram, as expected on a platinum surface. This figure represents the catalytic component arising only out of Pt nanoparticles. The choice of the above potential range ensures elimination of the effect of oxide in the voltammetric response.

Figures 7 and 8 refer to the impedance spectra obtained for the thin film electrode recorded at a potential of 0.3 V (kinetic-diffusion region) and 0.11 V (diffusion-control region) respectively. The spectrum recorded at 0.3 V shows a mixed control behaviour (kinetic and mass transport control) and the one at 0.11 V corresponds to diffusion control.

From the results discussed so far, a new method for the formation of Pt thin films through wet chemical method is demonstrated in this work. Its characterization and evaluation for electrocatalysis of small molecules like methanol that are relevant to fuel cell reactions are illustrated in this work. Dendrimers possess tens to hundreds of functional groups at the periphery, and the aggregate strength of these

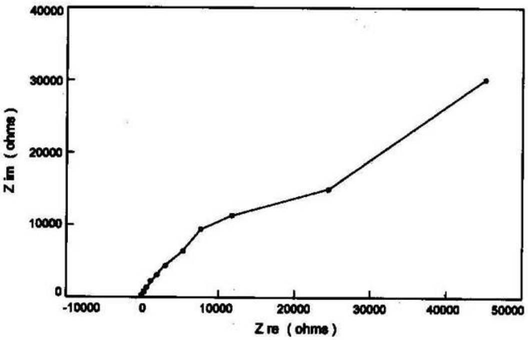

Figure 7. Impedance spectrum recorded at a potential of 0.3 V in the frequency range 10 mHz to 100 kHz.

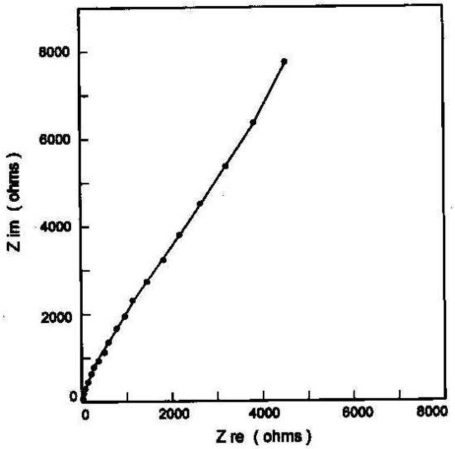

Figure 8. Impedance spectrum recorded at a potential of 0.11 V in the frequency range 10 mHz to 100 kHz.

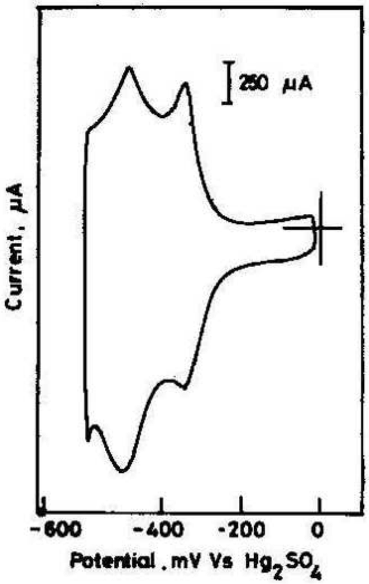

Figure 9. Cyclic voltammogram showing the hydrogen adsorption region recorded in 0.5 M H_2SO_4 at a scan rate of 50 mV/s.

multidentate interactions with metal atoms renders them a suitable choice for enhancing adhesion. Hence dendrimer molecules are preferable as adhesion promoters as each dendrimer molecule offers a number of chelating points when compared to conventional adhesion molecules with a limited number of chelating centers. They are expected to be more stable than the other well-known adhesion promoters like organosilanes, the hydrolysis of which leads invariably to unwanted siloxane formation. In the absence of dendrimers, less stable films that can easily be *peeled off* are formed on gold surfaces. Hence, the dendrimer molecules help in producing stable and adherent films on gold surfaces. The films produce similar catalytic currents even after a month.

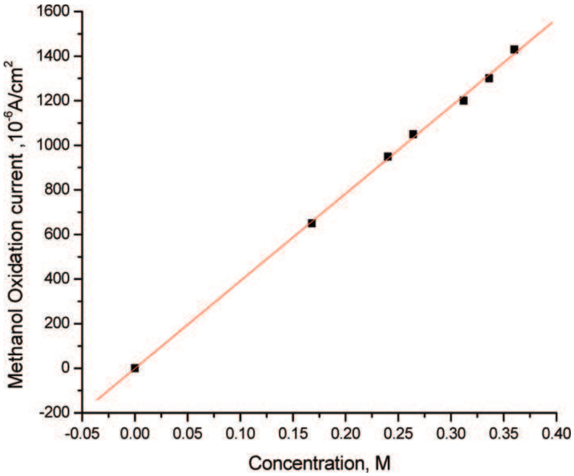

Figure 10. A plot of methanol oxidation current vs. concentration.

The surface morphology of the film as seen by AFM and SEM indicates that the particles are nucleated at different positions and therefore appear widely distributed instead of forming a uniform film. As the area focussed is restricted to 2000 nm × 2000 nm in the AFM analysis, agglomerated particles rather than the distribution of particles is seen. This shows that each nucleating centre constitutes a heavy load of Pt concentrated into the dendrimer molecule. Interestingly, the hydrogen adsorption values are quite high compared to the polycrystalline Pt of the same geometric area, which reflects a very high surface of dendrimer-derived Pt films (figure 9). Multidentate nature of dendrimer molecules leads to a high loading of Pt in the dendrimer-derived films and the particulate nature of the films increases the surface area. The hydrogen adsorption charge works out to be 1.25 mC/cm^2 and is very high relative to a monolayer charge of $\sim$210 μC/cm^2, higher than that observed for polycrystalline bulk Pt electrodes yielding a value for roughness factor to be $\sim$5–6 [17].

Figures 5 and 6 are the cyclic voltammetric responses for methanol oxidation occurring on thin films of Pt. The peak characteristics are listed in tables 1 and 2. The onset of oxidation occurs at a very low potential and catalytic current density observed is also quite high, factors being greater than the roughness factor calculated using the ratio of the hydrogen adsorption charge of dendrimer-derived film to the smooth platinum electrode [17]. The methanol oxidation currents recorded at different concentrations are found to linearly vary with the concentration of methanol (figure 10). This indicates that this method also provides scope for developing an analytical protocol for amperometrically sensing methanol in the range of methanol concentrations used in this work.

From the impedance spectra, it is clear that though both the peaks occurring at 0.3 V and 0.1 V represent methanol oxidation, their impedance spectra are kinetically quite different. At 0.3 V, the methanol oxidation appears to be under the mixed control of kinetics and mass transfer whereas at 0.1 V, the oxidation is under diffusion control. The R_{ct} associated with the methanol oxidation at 0.3 V is very high (25 to 30 kΩ).

Table 1. Peak characteristics of methanol oxidation observed in the forward scan in 0.5 M H_2SO_4.

Concentration of methanol (M)	Onset of methanol oxidation (V)	Peak potential (V)	Peak current (μA)	Peak current density (μA/cm^2)
0.017	−0.25	0.31	800	1600
0.034	−0.25	0.32	1540	3080
0.051	−0.25	0.33	1580	3160
0.068	−0.25	0.33	1900	3800
0.085	−0.25	0.33	2100	4200
0.25*	0.39	0.64	–	210

*Values reported by Abruna *et al* [17]. Potentials are with respect to Ag/AgCl.

Table 2. Peak characteristics of methanol oxidation observed in the reverse scan.

Concentration of methanol (M)	Peak potential (V)	Peak current (μA)	Peak current density (μA/cm^2)
0.017	0.05	640	1280
0.034	0.06	1020	2040
0.051	0.06	1160	2320
0.068	0.07	1460	2920
0.085	0.07	1520	3040

4. Summary

This method describes a novel method for the preparation of thin films of Pt by a wet chemical method. This entails use of multidentate dendrimer molecules as adhesion promoters for deposition on gold surfaces. The surface morphology of the film indicates that the surface consists of Pt particles widely spaced and size ranges from 200 to 300 nm. Multidentate nature of dendrimer molecules leads to high loading of Pt in the dendrimer-derived films and the particulate nature of the films increases the surface area. As a result, these films are found to have high catalytic activity towards methanol oxidation compared to bulk platinum. The films are found to be very stable with catalytic currents reproducible even after a month.

References

[1] Z Jusys, J Kauser and R J Behm, *Langmuir* **19**, 6759 (2003)
[2] W Lu, G Q Chrzanocoski and A Wieckowski, *J. Phys. Chem.* **B104**, 5566 (2000)
[3] K Jambunathan, S Jayaraman and A C Hiller, *Langmuir* **20**, 1856 (2004)
[4] A Chen, D J La Russa and B Miller, *Langmuir* **20**, 9695 (2004)
[5] S Park, Y Xie and M J Weaver, *Langmuir* **18**, 5792 (2002)

[6] G Larsen, E Lotero and M Marquez, *J. Mater. Res.* **15**, 1842 (2000)
[7] G Larsen, E Lotero and M Marquez, *J. Phys. Chem.* **B104**, 4840 (2000)
[8] M R Knecht and D W Wright, *Langmuir* **20**, 4728 (2004)
[9] M R Knecht and D W Wright, *Chem. Mater.* **16**, 4890 (2004)
[10] R M Crooks, M Zhao, L Sun, V Checkik and C K Yeung, *Acc. Chem. Res.* **34**, 181 (2001)
[11] M Zhao, L Sun and R M Crooks, *J. Am. Chem. Soc.* **120**, 4877 (1998)
[12] Y Niu, L K Yeung and R M Crooks, *J. Am. Chem. Soc.* **123**, 6840 (2001)
[13] Y Li and M A El Sayed, *J. Phys. Chem.* **B105**, 8938 (2001)
[14] R W J Scott, A Datyc and R M Crooks, *J. Am. Chem. Soc.* **125**, 3708 (2003)
[15] R W J Scott, O M Wilson, S K Oh, E A Kenik and R M Crooks, *J. Am. Chem. Soc.* **126**, 15583 (2004)
[16] E Casado-Rivera, D J Volpe, L Alden, C Lind, C Downie, T V Alvarez, A C D Angelo, F J DiSalvo and H D Abruna, *J. Am. Chem. Soc.* **126**, 4043 (2004)
[17] A J Bard and L R Faulkner, *Electrochemical methods – fundamentals and applications* (John Wiley, New York, 2004) p. 560