Preparation of Chemically Modified Electrodes by Attachment of Platinum Carbonyl Clusters, and their Efficient Electrocatalytic Action in Anodic Oxidation of Methanol

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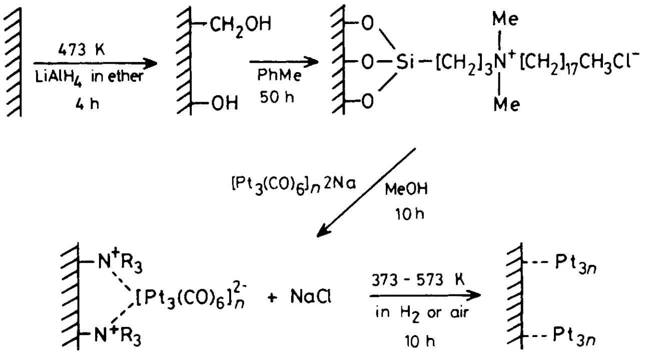
Chemically modified electrodes, prepared by impregnating surface-modified graphite discs and anion-exchange membranes with $[Pt_3(CO)_6]_n{}^{2-}$ (n = 3 or 5; platinum carbonyl cluster anions) by an ion-exchange technique, provide higher specific electrocatalytic activities for the anodic oxidation of methanol than conventional platinum electrodes.

Chemical modification of electrode surfaces has been of recent interest, with a view to the sophisticated control of electrochemical processes.[1] Some organometallic compounds such as Fe–S clusters[2] and metalloporphyrins[3,4] have been used to generate novel redox systems. Recently, much attention has been paid to organometallic cluster compounds as precursors of metal aggregates of uniform size and composition, highly dispersed on metal oxides or carbon.[5] The present paper deals with the preparation of platinum cluster-attached electrodes and their electrocatalytic properties for the anodic oxidation of methanol.

Platinum carbonyl cluster complexes, $Na_2[Pt_3(CO)_6]_n$ (n = 3 or 5), were prepared by Chini's method.[6] Surface-modified graphite discs (4 mm diam. × 2 mm; Union Carbide Co., L3804 AGKSP) and anion-exchange membranes of the type $-[(CF_2)_{2m+1}-CF\ (N^+R_3Cl^-)]_n-$ with an exchange capacity of 0.81 mmol equiv g^{-1} solid (EA-45; Toyo Soda Kogyo Co.) were employed as electrode substrates. The surface modification of the graphite[1—3,7,8] was carried out as shown in Scheme 1 with dimethyl(octadecyl)-[3-(trimethoxysilyl)propyl]ammonium chloride and by attachment of platinum carbonyl cluster complexes.

The resulting electrodes were examined by means of Auger electron spectroscopy. Auger patterns of the specimens consisted of main peaks corresponding to Pt (66 eV), Si (92 eV), Cl (180 eV), C (273 eV), and O (503 eV); those of N and Na were not observed. A series of high resolution electron microscopic observations[9] of Rh_6/Al_2O_3 and Pt_{15}/SiO_2 specimens have suggested that the rhodium and platinum aggregates prepared are indeed of a size in keeping with an entity of the starting rhodium and platinum carbonyl cluster compounds.

The electrochemical measurements were carried out potentiostatically in 0.5 M-H_2SO_4 solution containing 1.0 M-MeOH at 303 K under a stream of argon in a conventional three-compartment glass cell. Electrical contact to the electrodes was made by holding them on tantalum lead wires in the case of the platinum cluster-attached graphite discs (Pt_{3n}/C) or placing between gold meshes in the case of the anion-exchange membranes (Pt_{3n}/M). The quantity of platinum atoms attached to the electrode surface was evaluated from the quantity of electricity required to remove hydrogen atoms on platinum by oxidation in the potential range of 0.05—0.40 V assuming, as usual, that hydrogen is adsorbed on the surface platinum atoms in the ratio H : Pt = 1 : 1.



Scheme 1

The observed anodic currents of methanol oxidation per unit surface of platinum atoms are summarized in Table 1, together with those on conventional platinized Pt electrodes (Pt_∞) and on carbon-supported platinum electrodes prepared by platinum impregnation with platinum(IV) chloride acid (Pt_x/C).

The dependence of the rate of anodic oxidation of methanol at 0.60 V (*vs.* reversible hydrogen electrode) on the temperature of heat treatment for Pt_{15}/C and Pt_{15}/M electrodes is shown in Figure 1. The Pt_{15}/M electrode showed a higher electrocatalytic activity than conventional platinum electrodes. The Pt_{15}/C electrodes before heat treatment had an activity about ten times lower than that of Pt_{15}/M, but considerably enhanced by raising the heating temperature, and eventually approaching to that of the Pt_{15}/M electrode. The heat treatment was more effective in an oxidizing atmosphere (air) than in H_2.

It has been reported previously that specific electrocatalytic

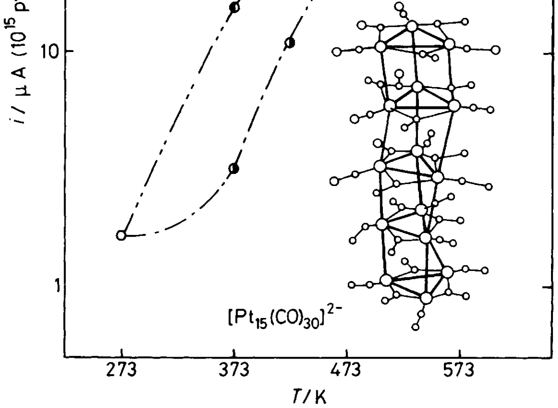


Figure 1. Specific electrocatalytic activity *vs.* heat-treatment temperature of Pt_{15}/C and Pt_{15}/M electrodes. The ordinate shows the anodic oxidation of methanol in 0.5 M-H_2SO_4 containing 1.0 M-MeOH at 0.60 V (*vs.* reversible hydrogen electrode) and 303 K; inset: the molecular structure of $[Pt_{15}(CO)_{30}]^{2-}$.

Table 1. Electrocatalytic activity of platinum cluster-attached and conventional platinum electrodes for the anodic oxidation of methanol in 0.5 M-H_2SO_4 containing 1.0 M-MeOH at 303 K.

Pt unit	Substrate[a]	Treatment	i[b]/μA (10^{15}Pt)$^{-1}$
Pt_9	C	None	0.32
		H_2, 423 K, 10 h	4.50
		Air, 423 K, 10 h	14.0
Pt_{15}	C	None	1.70
		H_2, 423 K, 10 h	11.0
		Air, 423 K, 10 h	28.8
Pt_{15}	M	None	29.2
		H_2, 473 K, 10 h	38.5
Pt_∞[c]		None	1.5—4.0
Pt_x[d]	C	H_2, 573 K, 10 h	10.1
		H_2, 573 K, 10 h Air, 423 K, 5 h	9.5

[a] C and M represent graphite discs and anion-exchange membranes, respectively. [b] Oxidation current at 0.60 V *vs.* reversible hydrogen electrode. [c] Platinized Pt with a roughness factor of *ca.* 120. [d] These samples were prepared by impregnating platinum(IV) chloride acid on the hydrated graphite disc substrates. The size of platinum particles is deduced to be in the range 30—100 Å from the ratio of surface platinum to total supported platinum.

activity of dispersed platinum aggregates of size 15—35 Å, prepared by vacuum evaporation, decreases monotonically with decrease in platinum particle size.[10] In contrast, the present results suggest that the platinum aggregates (Pt_9 and Pt_{15}) derived from platinum carbonyl cluster anions of less than 10 Å (suggested by high resolution electron microscope observations[9]) are still active, and even more active than the conventional platinum electrode, for the anodic oxidation of methanol. Further investigations are required before a quantitative relation between electrocatalytic activity and the platinum particle size can be established.

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