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PRECISE CONTROL OF AMOUNT OF ELECTRODEPOSITED Pt BY USING THE LANGMUIR-BLODGETT FILM AND ITS APPLICATION TO ELECTROCATALYSIS OF MOLECULAR OXYGEN REDUCTION

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The amount of Pt deposited on a glassy carbon (GC) electrode can be controlled precisely by electrochemical reduction of $PtCl_6^{2-}$ incorporated as a counter ion in the Langmuir-Blodgett (LB) film coated on the electrode surface. Electrocatalysis of the resulting modified electrode for molecular oxygen reduction is also described.

In the last decade, the chemical modification of electrode surfaces has been intensively investigated as a means for making various functional electrodes.[1)] Among them, the acceleration of molecular oxygen reduction[2)] has been studied extensively in connection with fuel cells. However, noble metals such as Pt still have been the highest and the most stable catalyst. The electrochemical behavior has been reported for transition metal complexes bearing charges opposite to that of the polyelectrolyte coated on graphite electrodes.[3)] Several groups have developed the research to a modified electrode with Pt dispersed in a polymer film coated on the electrode surface.[4)] However, the mass transfer of substrates through the polymer film can be rate determining.[4)] In addition, minimization of the amount of noble metal is impelled by the high cost of such materials.

Two kinds of cationic surfactants with two long alkyl chains were tested for LB films: the electroactive viologen surfactant EPADOV, N-ethyl-N'-[3-propylamido-N",N"-di(n-octadecyl)]-4,4'-bipyridinium dibromide[5)] and the electroinactive quaternary ammonium salt DODAC, dioctadecyldimethylammonium chloride. Each monolayer was prepared by spreading its dilute chloroform solution (0.1 mM for EPADOV and 1mM for DODAC) on a surface of an aqueous subphase containing 0.03 mM H_2PtCl_6 in a Langmuir trough (Kyowa Kaimenkagaku Co.). Both surfactant monolayers were deposited on GC electrodes as Z-type films at 35 dyn cm^{-1}.

A cyclic voltammogram of the reduction of $PtCl_6^{2-}$ confined as a counter ion in the LB film of EPADOV is shown in Fig. 1. The number of dips tried for the LB film deposition ranged from one to eight. The amount of charge passed Q, calculated from the surface wave increased linearly with an increase in the number of dips as is evident from Table 1, where are also listed Pt

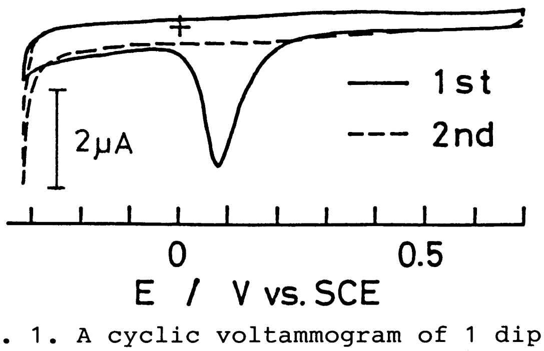

Fig. 1. A cyclic voltammogram of 1 dip coating of EPADOV LB film with $PtCl_6^{2-}$ in 0.1 M H_2SO_4 under N_2 (50 mV s^{-1}).

Table 1. Charge for reduction of Pt complex in EPADOV LB films coated on GC electrode and Pt loading calculated therefrom.

Dip	Charge Q μC	Pt from Q ng cm^{-2}	Pt from Γ ng cm^{-2}
1	6.2	49	60
2	12.4	97	120
3	19.0	150	180
4	25.8	204	240
8	44.6	350	480

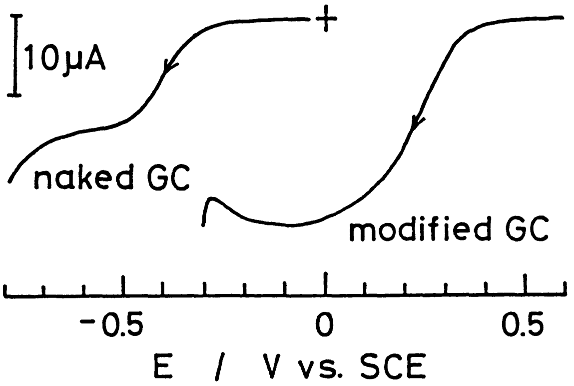

Fig. 2. i - E curves for air-saturated 0.1 M H_2SO_4 on rotating disk electrodes.

loadings calculated from Q and those from the surface concentration Γ of EPADOV at 35 dyn cm^{-1} on the assumption that one monolayer was transferred exactly on each dipping. These values are in fair agreement with each other. The experimental findings here leads to an important conclusion that the precise control within ca. 10 ng cm^{-2} of a small amount of deposited noble metals on carbonaceous materials can be attained by the present method. The adsorbed hydrogen and oxygen waves on deposited Pt became more apparent with an increase in the number of dips and their shape and quantity will be related to the size and state of Pt. It is interesting to compare Pt microdeposited in this work with Pt ad-atoms.[6]

In Fig. 2 are shown the current - potential (i - E) curves for oxygen reduction on rotating disk electrodes (400 rpm) with a naked GC surface and the modified GC surface with Pt loaded similarly from 2 dips of DODAC with $PtCl_6^{2-}$. A positive shift of ca. 0.7 V of the onset potential and the current doubling for oxygen reduction were observed by the modification. This indicates that oxygen was reduced into water, because the reduction product on the naked GC electrode was known to be H_2O_2[2a], and also that the LB overlay was so thin (≈10 nm) that the reduction was not limited by the mass transfer of oxygen through the film.

The present method will be applicable widely for deposition of other various metals and for preparation of ultrafine metal particles.

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