

Interfacial crystallization and electronic properties of platinum double salts

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Insoluble platinum double salts were crystallized by a novel method involving a solid-liquid interface. The platinum complexes included Magnus Green Salt, MGS ($[\text{Pt}(\text{NH}_3)_4]^{2+} [\text{PtCl}_4]^{2-}$) and PBC ($[\text{Pt}(\text{bpy})_2]^{2+} [\text{Pt}(\text{CN})_4]^{2-}$). The crystallization and molecular ordering of MGS and PBC on a Nafion membrane were achieved by controlling the diffusion of the cation and anion components to the solid-liquid interface. The electrical conductivity of the MGS film on Nafion was greatly augmented by oxidizing the polynuclear complex. A device consisting of the PBC film on Nafion, methyl viologen, and triethanolamine displayed photoelectrochromism.

1. Introduction

Thin films of polynuclear transition metal complexes on a solid polymer support show interesting electrochemical properties applicable to rechargeable batteries and electrochromic displays [1-3]. Partial oxidation of the linear chain platinum complex Magnus Green Salt, MGS ($[\text{Pt}(\text{NH}_3)_4]^{2+} [\text{PtCl}_4]^{2-}$), produces the mixed-valence state of the complex, and six orders of magnitude increase in electrical conductivity [4-6]. Another linear chain platinum double salt, PBC ($[\text{Pt}(\text{bpy})_2]^{2+} [\text{Pt}(\text{CN})_4]^{2-}$, bpy = 2,2'-bipyridine), photosensitizes H_2 evolution from water [7]. Many of these platinum complexes are, however, difficult to process as either thin films or ultra-fine particles. Using an approach developed earlier [1], we have succeeded in preparing thin crystalline films of MGS and PBC on Nafion (Nf). In this paper, we describe the interfacial crystallization and electrochemical characterization of MGS, PBC, and several related platinum complexes.

2. Experimental details

2.1. Chemicals

Nafion 117 (Aldrich Chemical Company; thickness $\sim 180 \mu\text{m}$) was cleaned by boiling for 3 h in concentrated HNO_3 and then soaking for 3 h in distilled water. The platinum salts ($[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$, $\text{K}_2[\text{PtCl}_4]$, $\text{K}_2[\text{PtCl}_6]$, $\text{K}_2[\text{PtBr}_4]$, and $\text{K}_2[\text{Pt}(\text{CN})_4]$) were used as-received from Soekawa Chemical Co. The complex $\text{K}_2[\text{Pt}(\text{bpy})_2](\text{NO}_3)_2$ was prepared as described elsewhere [7].

2.2. Interfacial crystallization of platinum complexes on Nafion

A $2 \text{ cm} \times 2 \text{ cm}$ Nf membrane was immersed in an aqueous 100 mM $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ solution for 2 h and then rinsed repeatedly with distilled water. Next the Nf was partially dried by sandwiching it between two sheets of filtration paper. The membrane was then immersed in an aqueous 100 mM $\text{K}_2[\text{PtCl}_4]$ solution for 2 h. This procedure produced a green crystalline film of MGS on the surface of the Nf membrane. This film could easily be detached from the wet Nf by wiping, but adhered strongly to the dry membrane. Except for PBC, the other platinum double salts were prepared in a similar manner.

PBC films on Nf were prepared as follows: Nf was immersed successively in aqueous solutions of 25 mM $\text{K}_2[\text{Pt}(\text{bpy})_2](\text{NO}_3)_2$ and 25 mM $\text{K}_2[\text{Pt}(\text{CN})_4]$ for 2 h each. The crystalline film that formed on the surface of Nf turned from orange to red when dried. This colour change, which depends on the extent of hydration [7], was reversible. The thickness of the films, which was generally about $1 \mu\text{m}$, varied with the concentration of the cation and anion components and the amount of time allowed for crystal growth. The morphology of the MGS and PBC films on Nf was examined by scanning electron microscopy (SEM, Jeol, Model JSM-T100).

2.3. Chemical and electrochemical oxidation of MGS

The MGS-Nf composite film was immersed in an

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aqueous solution containing 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ /1.0 M NaClO_4 , 0.1 M H_2O_2 /1.0 M HClO_4 , or 0.05 M $\text{Ce}(\text{SO}_4)_2$. The colour of the film changed from green to copper red when the material was chemically oxidized. The electrical conductivity of the composite film was measured after the film was washed with water and dried *in vacuo*. Either the four-point probe or the two-point probe method was used for the conductivity measurements, depending on the magnitude of the resistivity of the samples.

The structural change, associated with the chemical oxidation of MGS, was analysed using an infrared spectrophotometer. The MGS film, after oxidation with $\text{Na}_2\text{S}_2\text{O}_8$, was dried and then dispersed in KBr pellets for infrared (IR) measurements.

The MGS particles were suspended in a conductive carbon paint by sonication. The suspension was then coated on to a glassy carbon electrode. The two-compartment electrochemical cell used for cyclic voltammetry contained argon-purged aqueous 1 M NaClO_4 solution, the glassy carbon working electrode, a platinum wire counter electrode, and a saturated NaCl calomel reference electrode (SSCE).

2.4. Photoelectrochemical characterization of PBC

The PBC-Nf composite film was immersed in an aqueous 10 mM methyl viologen dichloride (MV^{2+}) solution for 2 h. A cellulose filter paper wetted with an aqueous 1 M triethanolamine (TEOA) solution was overlaid on the PBC-Nf film to form an MV^{2+} -containing PBC-Nf composite structure. The Nf surface of the double-layered film was irradiated with light from a 650 W tungsten-halogen lamp. The incident light intensity on the sample was approximately 200 mW cm^{-2} ; a water filter was used to remove IR radiation. A differential reflectance spectrum of the film was obtained before and after irradiation. A multichannel photodetector (Ohtsuka Electronics Co., Model MCPD 200) was positioned at a 45° angle to the front surface of the Nf membrane.

3. Results and discussion

3.1. Interfacial crystallization of MGS and PBC on Nafion

MGS and PBC were obtained, respectively, by mixing aqueous solutions containing equal concentrations of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ with $[\text{PtCl}_4]^{2-}$ and $[\text{Pt}(\text{bpy})_2]^{2+}$ with $[\text{Pt}(\text{CN})_4]^{2-}$. The formation of these platinum double salts was more rapid in homogeneous media than at the Nf-liquid interface. The colours of the complexes on Nf were about the same as those obtained in solu-

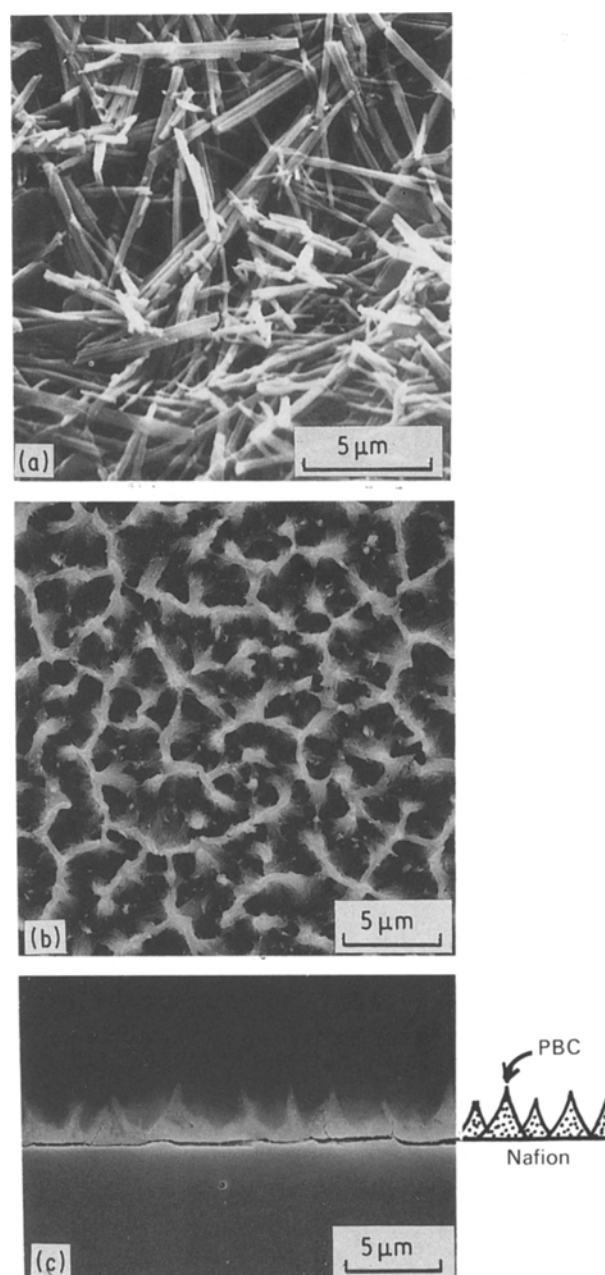


Figure 1 Scanning electron micrograph of the surface of Nafion films on which platinum double salts are deposited. (a) MGS/Nf; (b) PBC/Nf; (c) a cross-section of PBC/Nf.

tion; the MGS and PBC films were green and orange, respectively, when wet. The PBC film turned red when dehydrated. The scanning electron micrographs in Fig. 1 demonstrate that MGS and PBC grew as crystalline needles on Nf. The crystals of MGS were larger than those of PBC, however. The other platinum complexes, listed in Table I, also grew as needles. The

TABLE I Electrical conductivity (σ) and colour characteristics of thin films of platinum complexes on Nafion

Sample		Before oxidation		After oxidation*	
Abbreviation	Composition	Colour	σ (S cm^{-1})	Colour	σ (S cm^{-1})
A (MGS)	$[\text{Pt}(\text{NH}_3)_4]/[\text{PtCl}_4]$	Green	1×10^{-5}	Copper red	1×10^0
B	$[\text{Pt}(\text{NH}_3)_4]/[\text{PtCl}_6]$	Green	4×10^{-6}	Copper red	2×10^{-1}
C	$[\text{Pt}(\text{NH}_3)_4]/[\text{PtBr}_4]$	Yellowish green	8×10^{-8}	Brown	2×10^{-7}
D	$[\text{Pt}(\text{NH}_3)_4]/[\text{Pt}(\text{CN})_4]$	White	3×10^{-8}	Yellowish brown	2×10^{-7}
E (PBC)	$[\text{Pt}(\text{bpy})_2]/[\text{Pt}(\text{CN})_4]$	Orange	9×10^{-7}	Orange	2×10^{-6}
F	$[\text{Pt}(\text{bpy})_2]/[\text{PtCl}_4]$	Reddish yellow	6×10^{-7}	Reddish yellow	5×10^{-7}

*The oxidation of platinum complexes on Nf involved immersing the film in an aqueous 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ /1 M NaClO_4 solution for 3 min.

long axes of the PBC crystals grew perpendicular to the Nf surface, whereas MGS crystals formed on randomly to the surface. The size and orientation of the crystals grown on Nf depended on the diffusion of the monomeric ions to the solid interface and on the molecular packing behaviour of the ions.

3.2. Electrical conductivities of platinum complexes

The conductivity of MGS particles can be increased from 10^{-5} to 10^{-1} S cm^{-1} by partial oxidation of platinum with chemical reagents, such as O_2 and Pt(IV) [4–6]. Table I shows the conductivity and colour of the films of the platinum complexes on Nf before and after chemical oxidation with $\text{S}_2\text{O}_8^{2-}$. On oxidation of MGS and complex B, the conductivity increased by five orders of magnitude. As the conductivity increased, the colour of MGS and complex B changed from green to copper red. On oxidation, the conductivity of complexes C and D, increased relatively little, although their respective colours changed from yellowish green to brown and white to yellowish brown. These observations indicate that complexes C and D underwent a chemical change when they were exposed to persulphate. The white colour of complex D suggests very little, if any, Pt–Pt interaction in the material. PBC and complex F showed neither an increase in conductivity nor a colour change in the presence of persulphate. Both complexes appeared resistant to chemical oxidation, presumably because of the strong coordination bonding between bpy and platinum and/or steric effects associated with the ligand.

3.3. Chemical oxidation characteristics of MGS films

Fig. 2 shows the conductivity changes with time when MGS/Nf is exposed to chemical oxidants. The conductivity of the MGS film in $\text{S}_2\text{O}_8^{2-}$ or H_2O_2 solution increased from 1×10^{-5} to 10^0 S cm^{-1} and then declined; concomitant with the conductivity change, the complex turned from green to copper red.

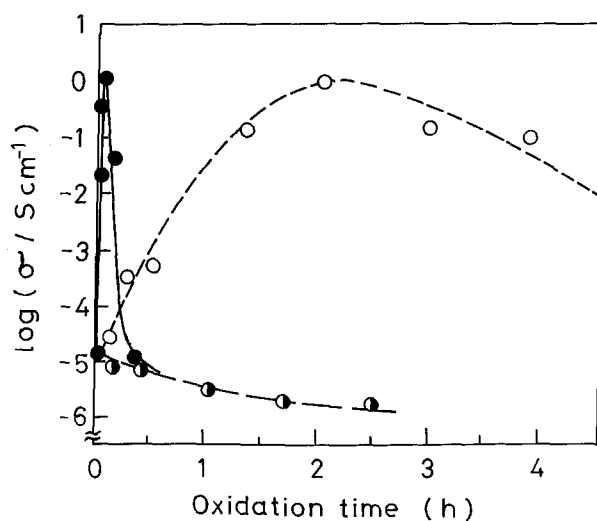


Figure 2 Room-temperature dependence of the conductivity of MGS/Nf on time when the film is exposed to several oxidants. (●) $0.1 \text{ M Na}_2\text{S}_2\text{O}_8/1.8 \text{ M NaClO}_4$, (○) $0.1 \text{ M H}_2\text{O}_2/1.0 \text{ M HClO}_4$, (◐) $0.05 \text{ M Ce(SO}_4)_2$.

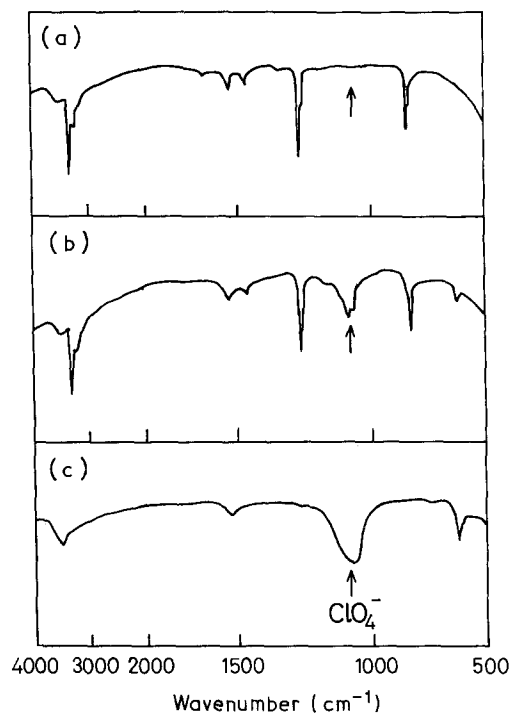


Figure 3 IR spectra of MGS on Nf before and after oxidation with $0.1 \text{ M Na}_2\text{S}_2\text{O}_8/1.0 \text{ M NaClO}_4$; (a) before oxidation, (b) 15 sec after oxidation, and (c) 8 min after oxidation.

Cerium(IV) had little effect on the conductivity of the MGS film.

Fig. 3 shows IR spectra of MGS/Nf before and after immersing it in a $\text{Na}_2\text{S}_2\text{O}_8$ solution. The characteristic stretching and bending vibrational modes of N–H [8] are still evident after 15 sec exposure of MGS to the oxidant (Fig. 3b). The new band at 1140 cm^{-1} in spectrum b is attributed to the uptake of perchlorate anions in the film [9]. The perchlorate anion is presumed to compensate the excess positive charge in the MGS matrix, owing to the oxidation of platinum atoms along the chain axis. When further oxidized, MGS decomposes as suggested by Fig. 3c, which shows the near absence of the N–H vibrational modes.

The oxidative behaviour of MGS was further characterized electrochemically. Fig. 4 shows cyclic voltammograms of MGS particles dispersed in a carbon paint on the surface of a glassy carbon electrode. An anodic peak and a cathodic peak were observed at 0.86 and 0.50 V , respectively, when the potential was cycled between -0.30 and 0.90 V (Fig. 4a). The peak currents of this redox reaction gradually decreased with repeated potential scans. This behaviour is attributed to the irreversible oxidation of MGS. On voltage excursions to 1.20 V , an anodic peak and a cathodic peak appeared at 0.98 and 0.40 V , respectively (Fig. 4b). On repeated potential scans, the peak current decreased rapidly, indicating the decomposition of the MGS film. Although MGS can be reversibly oxidized, it is known to undergo irreversible oxidation and decomposition at oxidation potentials greater than 0.65 V [10].

3.4. Photoelectrochemical reaction of PBC film on Nafion

Aqueous PBC suspensions, when illuminated with

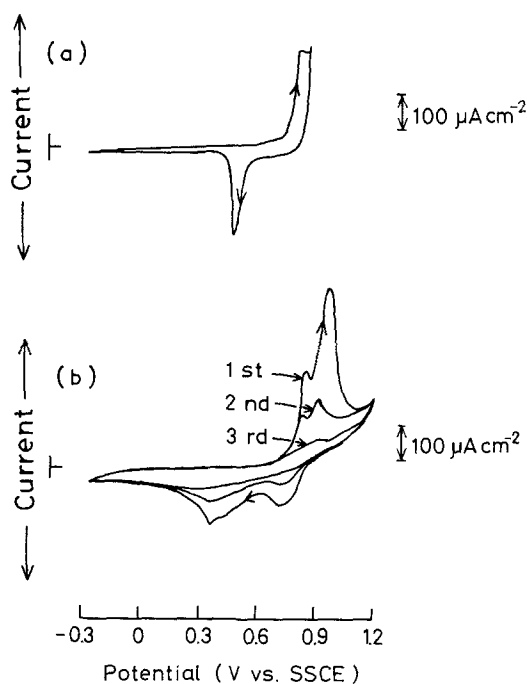


Figure 4 Cyclic voltammograms of MGS-coated glassy carbon electrode in an aqueous 1 M NaClO₄ solution; scan rate of 50 mV sec⁻¹. (a) Potential sweep between -0.30 and 0.90 V, (b) potential sweep between -0.30 and 1.20 V.

visible light, in the presence of platinum colloids and an electron donor, photosensitive H₂ evolution from water [7]. Other platinum complexes, such as Prussian Blue in the presence of the photoreceptor CdS and an electron donor, exhibit photoelectrochromism [11–13]. One of the problems encountered in such a system is the photocorrosion of the semiconductor photoreceptor. PBC was found to be more stable than CdS in such a photoelectrochromic system.

The photoreduction of MV²⁺ by PBC on Nf in the presence of the electron donor TEOA was investigated. Fig. 5a shows a differential reflectance spectrum of the PBC-MV²⁺-TEOA/Nf composite membrane before and after 30 min visible light irradiation; the temporal dependence of the reflectance at 600 nm is shown in Fig. 5b. The membrane, when illuminated, turned from orange to bluish purple. The reflectance spectrum in Fig. 5a is almost identical to that obtained by electrochemical reduction of MV²⁺ in the absence of PBC. The colour change produced by illumination is thus attributed to the reduction of MV²⁺ to the MV^{•+} radical cation. The colour of the membrane changed back from bluish purple to orange when the film was exposed to air. The photo-induced electrochromism did not occur in the absence of either PBC or TEOA. An action spectrum of the photocurrent for PBC-MV²⁺-TEOA/Nf showed an onset around 600 nm in good accord with the diffuse reflectance spectrum of the PBC film. From these studies, we infer that the photoelectrochromism displayed by the PBC-MV²⁺-TEOA/Nf film involves the light-activated electron transfer from PBC to MV²⁺.

The MGS film on Nf was photo-inactive toward the reduction of MV²⁺ under similar conditions used for PBC/Nf. However, MGS changed, when illuminated, from green to dark brown. The reflectance

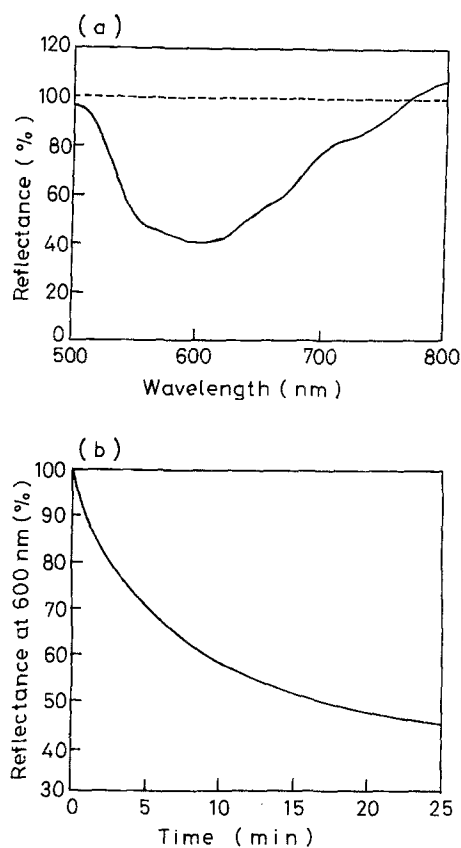


Figure 5 Surface reflectance of the illuminated PBC-MV²⁺-TEOA/Nf composite film. (a) Differential spectrum before and after the irradiation of film for 30 min, and (b) time dependence of reflectance at 600 nm.

spectrum of MGS after irradiation was altered irreversibly in contrast to the situation involving PBC/Nf (Fig. 5a). These results suggest that MGS in the presence of MV²⁺ decomposes under irradiation. We speculate that the [Pt(bpy)₂]²⁺ component plays an important role in the reduction of MV²⁺ and that the [Pt(CN)₄]²⁻ component acts as a stabilizing influence against photo-induced decomposition; the chloride ligand is more labile than cyanide [7]. These studies thus indicate that PBC exhibits more favourable properties for photoelectrochromism than MGS.

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