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Synthesis and Electrocatalytic Properties of Rare Earth Platinum or Palladium Bronzes

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Synopsis. Dysprosium platinum and palladium bronzes, DyM_3X_4 (M=Pt or Pd; X=O, S, Se, or Te) were synthesized, except for $DyPt_3S_4$, by a solid state technique. They were found to have a high electric conductivity with $\rho=0.3$—$2.6\times10^{-5}\ \Omega$ cm and among them, the oxide bronzes crystallized in $Na_xPt_3O_4$ type structure. The platinum oxide bronzes in particular showed a high activity for the methanol electrooxidation as compared with ordinary platinum electrodes.

Metal bronzes can be candidates for electrode materials,[1)] since they often show a good electric conductivity and some of them possess a high corrosion resistivity in acid or alkali solutions. Shannon et al.[2)] have tested a series of $M'_xPt_3O_4$ (M′=Li, Na, Mg, Ca, Zn, Cd, Co, and Ni), and found them promising as brine electrolyzer anodes or H_2–O_2 fuel cell electrocatalysts. Recently, rare earth palladium sulfide analogues of the platinum oxide bronzes, $LnPd_3S_4$(Ln=rare earth elements), have been reported by Keszler and Ibers.[3)]

Methanol electrooxidation characteristics of platinum electrodes in acid solution are known to be considerably influenced by a trace amount of foreigen elements.[4)] Among them, rare earth elements, typically dysprosium, have been reported to possess a significant degree of activity enhancement effect on the reaction.[4c)] In this note, dysprosium platinum or palladium bronzes are prepared and the electric and electrocatalytic properties were studied.

Experimental

Preparation Method. The rare earth platinum (or palladium) bronzes were prepared by a solid state technique: Appropriate amounts of Dy_2O_3 and PtO_2 (or PdO) for oxygen bronzes or elemental Dy, Pt (or Pd), and X′ (X′=S, Se, or Te) for other chalcogenide analogues were mixed. The former was heated at 773 K under oxygen stream for 40 h and the latter in an evacuated silica tube at 1073 K for 60 h. A structural analysis of the samples prepared was performed by X-ray diffraction (XRD) using monochrmatized Mo *Kα* radiation (λ=0.70926 Å) and the atomic ratio was checked by X-ray fluorescent spectroscopy.

Electrical and Electrochemical Measurements. The electric resistivity of the sintered samples were measured using a four probe method in air at room temperature. The methanol electrooxidation experiments were carried out according to the method described elsewhere.[5)]

X-Ray Photoelectron Spectroscopy Measurements. The XPS signals were obtained with an ESCA VG-III apparatus using Al *Kα* radiation.

Results and Discussion

Preparation of Bronzes. The samples obtained were found to give powder XRD patterns different from those of the raw materials, except for the case of the Dy–Pt–S mixture. The XRD data have indicated that the oxides are crystallized in a $Na_xPt_3O_4$ type structure (cubic, *Pm3n*).[6)] Preparation of the rare earth platinum or palladium oxide bronzes is the first case reported in so far as we know. The XRD data are listed in Table 1 and the phase relations are summarized in Table 2, together with those of the other chalcogenide systems Dy–M–X′. Since the oxide samples have been mixed with the remaining Dy_2O_3 and Pt (or Pd and PdO) or the reaction has not been stoichiometrically achieved, they are expected to be of the form $Dy_xM_3O_4$ with $x\leqq1$ and not DyM_3O_4. The lattice constants of the platinum and palladium oxide bronzes were determined by a least-square treatment to be a=5.665(3) and 5.651(2) Å, respectively. The

Table 1. X-Ray Diffraction Data for $Dy_xM_3O_4$ (M=Pt, Pd)

hkl	$Dy_xPt_3O_4$			$Dy_xPd_3O_4$		
	d_0/Å	d_c/Å	I/I_0	d_0/Å	d_c/Å	I/I_0
110	3.997	4.000	17	3.978	3.996	33
200	2.851	2.833	13	2.810	2.826	17
210	2.538	2.534	100	2.527	2.527	100
211	2.319	2.313	22	2.311	2.307	22
220	2.009	2.003	13	2.000	1.998	16
310	1.792	1.791	13	1.789	1.787	11
222	1.637	1.635	17	1.632	1.631	28
320	1.571	1.571	35	1.568	1.567	28
321	1.513	1.514	17	1.511	1.510	17
400	1.414	1.416	9	1.411	1.413	17

Table 2. Lattice Constant and Specific Resistivity of the Product Phases Prepared from Dy : M : X = 1 : 3 : 4 Mixtures

X	Lattice constant/Å		$\rho/10^{-5}\ \Omega$ cm	
	Pt	Pd	Pt	Pd
O	a=5.665(3) Å[a)] (Dy_2O_3, Pt)	a=5.651(2) Å[a)] (Dy_2O_3, PdO, Pd)	1.9	2.6
S	(PtS)[b)]	a=6.646(2) Å[a)]	110	1.4
Se	Unknown	Unknown	1.0	0.8
Te	Unknown	Unknown	0.3	0.3

a) These are isostructural with $Na_xPt_3O_4$.[6)] Starting materials in parentheses remained as impurities. b) The phase is assigned according to the XRD powder file.[7)] observed fact that the lattice constant of the platinum oxide bronze is about 0.2% larger than that of palladium appears to be reasonable from the difference between their ionic radii.

The crystal structure of $Dy_xM_3O_4$ is shown in Fig. 1. Each Dy atom is located in the hole of M_3O_4 framework and is surrounded by 8 O atoms. The M_3O_4 framework consists of M–O bonds of which each M or O atom is linked to 4 O and 3 M atoms with 1.998—2.003 Å. Particularly, the M and O atoms form a coplanar square or a triangle configuration with O atoms and M, respectively, which allow the chemical bonds between M and O atoms via interactions of their dsp^2 and sp^2 hybrid orbitals, etc. These covalently bonded atom groups must be closely related to their electrical properties as described later.

For the sulfide systems, the Dy–Pt–S specimen gives only those XRD patterns which are derived from PtS. Thus, no bronze was likely to be formed under the experimental conditions employed. Exceptionally, however, the palladium sulfide bronze, $DyPd_3S_4$ was formed in a single phase, which did not contain starting materials as impurities. The crystal data [cubic, a=6.646(2) Å] corresponded with that of the lanthanum analogue [cubic, a=6.7394(1) Å][3] which is isostructural with $Na_xPt_3O_4$ as well as the above oxide bronzes.

On the other hand, the selenide and telluride specimens showed new XRD patterns (Table 3) which were not assigned as that of the $Na_xPt_3O_4$ type bronze nor of other selenides or tellurides of Dy, Pt, and Pd; their structures were not determined. However, since they showed a high electric conductivity characteristic of bronzes as described later and the atomic ratio determined by the X-ray fluorescent spectra agreed with that in the starting mixtures, the new XRD patterns might be derived from the DyM_3X_4 type bronzes.

Electric Conductivity. The specific resistivity data of the specimens are summarized in Table 2. They were found to be good electric conductors (ρ=0.3—2.6×10^{-5} Ω cm), except for the specimen in the Dy–Pt–S system (ρ=1.1×10^{-3} Ω cm). The results seem to be in harmony with their phase formations: The high conductivity is realized with the formation of bronzes whilie the Dy–Pt–S mixture [of which the major phase is PtS (semiconductor)] has low conductivity. Along this line, the formation of bronzes in the selenide and telluride systems may be suggested from their high conductivity, although their structure has not been identified by the XRD method.

X-Ray Photoelectron Spectroscopy. Typical XPS spectra of $Dy_xPt_3Se_4$ are shown in Fig. 2. The spectrum derived from Se 3 d electrons consisted of two bands at 52.8 and 57.1 eV, which might be assigned to those of Se^{2-} and Se^{4+} ions, respectively. The Pt 4f electrons gave two sets of XPS signals at 70.9—74.2 and 73.6—77.0 eV, which might be attributed to neutral Pt atoms and Pt^{2+} ions, respectively. Since H_2SeO_3 and Pt have never been detected on the XRD pattern of $DyPt_3Se_4$, such ionic species are likely to be formed only near the surface by hydrolysis with moisture in air. For the dysprosium, a broad band at about 153.0 eV was observed which might be originated from the 4d electrons of Dy^{3+} ions. Similar valence relations among the elements were also observed on the other bronzes. Thus, the DyM_3X_4

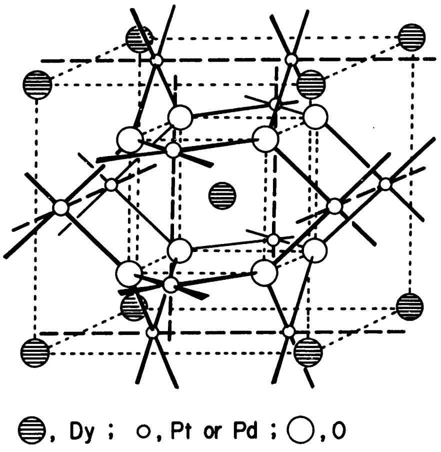

Fig. 1. Crystal structure of $Dy_xM_3O_4$ (M=Pt or Pd) based on the $Na_xPt_3O_4$ structure.[6]

Table 3. X-Ray Diffraction Data[a] for $DyPt_3X_4$ (X=Se, Te)

$DyPt_3Se_4$		$DyPt_3Te_4$	
d_0/Å	I/I_0	d_0/Å	I/I_0
7.53	5	11.95	12
5.47	68	5.94	100
5.10	100	5.26	51
3.81	4	3.96	6
3.42	6	2.959	5
3.28	10	2.907	21
3.24	8	2.856	42
2.996	14	2.594	5
2.935	15	2.396	9
2.780	21	2.140	12
2.730	60	2.094	16
2.673	13	2.042	13
2.646	13	1.998	7
2.552	8	1.745	5
2.471	13	1.658	5
2.384	6	1.576	13
2.344	15	1.560	7
2.093	6		
1.995	32		
1.924	5		
1.874	29		
1.815	46		
1.755	10		
1.699	5		

a) Similar XRD patterns were obtained for the $DyPd_3X_4$ bronze counterparts, respectively.

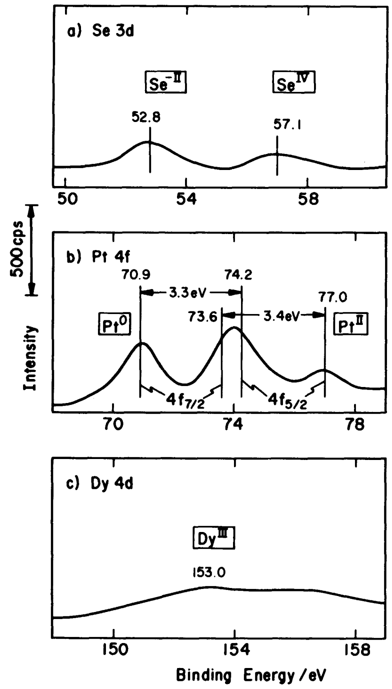

Fig. 2. X-Ray photoelectron spectra of Se 3d, Pt 4f, and Dy 4d electrons of $DyPt_3Se_4$.

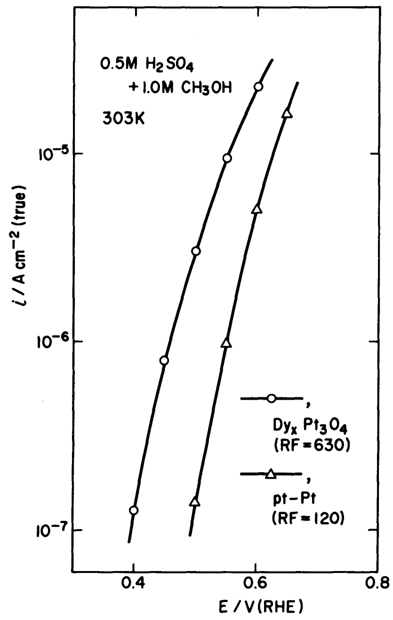

Fig. 3. Anodic polarization behaviours of the $Dy_xPt_3O_4$ and pt–Pt electrodes in methanol electrooxidation. *RF*: roughness factor.
0.5 M H_2SO_4+1.0 M CH_3OH, 303 K.

bronzes generally consist of the elements of Dy^{III}, M^{II}, and X^{-II}. Accordingly, these bronzes can generally be formulated as $[DyM_3X_4+e^-]$ and the resulting electrons are presumably sent to the conduction bands formed by the covalently bonded M_3O_4 framework. This model of supplying electrons can perhaps describe their metallic conductivity.

Methanol Electrooxidation Characteristics. The oxide bronzes, particularly $Dy_xPt_3O_4$, were found to have a high level of catalytic activity for the methanol electrooxidation. The other chalcogenide analogues were, however, unstable in acid solutions. The Tafel relation observed on a $Dy_xPt_3O_4$ electrode with the roughness factor (R_F; the value was determined by amounts of the under-potential hydrogen adsorption) of 630 is shown in Fig. 3, together with that of a platinized Pt (pt–Pt) electrode (R_F=120); the large R_F value of the bronze may be caused by the dissolution of one of the starting material, viz. Dy_2O_3, existed as an impurity in the bronze. The electrode showed the rest potential around 0.35 V (RHE) which was more negative, and hence suggested a better catalytic activity, than that of Pt itself at which it was usually 0.40—0.45 V. Indeed, the specific activity per true unit surface area of $Dy_xPt_3O_4$ was observed to be about one order of magnitude higher than that of ordinary Pt electrode.

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