CONDUCTION ELECTRON SPIN RESONANCE OF Pt-NANOPARTICLES IN POROUS Al₂O₃ MEMBRANES

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An electron spin resonance (ESR) investigation of Pt-nanoparticles electrodeposited in the channels of porous Al₂O₃ membranes has been performed in the temperature range 6 – 50 K. Pt – particle mean size was evaluated by means of Kawabata theory that relates ESR linewidth to metal particle size. A comparison with the effective crystallite mean size obtained from the X – ray diffraction analysis is given.

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1. Introduction

Anodic porous alumina (Al₂O₃) has recently attracted a great attention as a key material for fabrication of devices on a nanometric scale, such as electronic and photoelectronic devices and for application to micro- and ultrafiltration [1]. Also, nanoelectrode assembly can be obtained by using porous alumina as template.

Porous Al₂O₃ membrane includes numerous cylindrical nanopores (or channels) oriented in parallel to each other and having diameters as small as 11-13 nm [2]. These channels can be filled up with metallic materials by means of electrodeposition method.

Conduction ESR (CESR) spectroscopy is a powerful tool to study the magnetic behaviour and the electronic structure of small metallic particles [3]. It could also characterize their size according to the theory of Kawabata that relates CESR linewidth to metal particle size [4]. However, reliable experimental verification of this potentially useful theory is lacking and, therefore, a simple measure of small metallic particles size is of considerable significance [5].

To obtain further insight into the physical properties of small metallic particles, an CESR investigation of Pt – nanoparticle electrodeposited in self – assembled channels of porous Al₂O₃ membranes was carried out.

2. Experimental

Small Pt – metallic particles within the channels of Al₂O₃ membranes were produced by an electrodeposition method at room temperature using H₃PtCl₆ ( 10 mM ) in H₂SO₄ ( 0.2 M ) [6]. The electrodeposition time varied from 20 minutes to 1 hour. The investigated Pt / Al₂O₃ membrane (Pt 1) corresponds to 1 hour deposition time.

X– ray diffraction analysis of porous Pt/Al₂O₃ membrane was done by means of a standard DRON- 3M powder diffractometer.

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ESR measurements were carried out using a Brucker X-band spectrometer equipped with a helium gas-flow cryostat.

3. Results and discussion

The X-ray diffraction pattern of the electrodeposited membranes (Pt 1) is presented in Fig.1. It contains an intense (111) reflection indicating a textured membrane with (111) direction of the Pt type structure. The deposited metal has been confirmed to be Pt (face-centred cubic structure, fcc) with the lattice parameter $a_0 = 0.392$ nm.

![Fig. 1. X-ray diffraction pattern of Pt 1 sample.](image)

![Fig. 2. The crystallite size distribution as a function of the effective crystallite size along the perpendicular direction to the (111) planes (after Aldea and Indrea, 1990).](image)

Fig. 2 shows the crystallite size distribution function as determined from the second derivative of the strain corrected Fourier coefficients [7]. A value of $D_m = 9.7$ nm for the Pt – effective crystallite mean size could be evaluated by means of this function.

ESR measurements on Pt/Al$_2$O$_3$ membrane show one single line which we assign to an CESR signal of small Pt metallic particles showing quantum size effects. Within the whole temperature range (6 – 50 K) where the resonances were observed, the CESR lines are very asymmetric (Fig. 3). In order to fit the spectra we used an asymmetric Lorentzian function which includes both absorption and dispersion. The fit parameters are the half-width at half-height, $\Delta H_{1/2}$, of the corresponding absorption line and the resonance field, $H_0$.

![Fig. 3. ESR spectra of Pt/Al$_2$O$_3$ membranes.](image)

- $I_{ESR}$ (a.u.)
- $H$ (T)
- $I_{ESR}$ (a.u.)
- $T$ (K)

![Fig. 4. Temperature dependence of the ESR. The solid line corresponds to the Curie law giving the best fit to the data.](image)
The resulting CESR parameters $g = 2.092$ and $\delta H_{1/2} = 242$ Gs are independent of temperature and the asymmetry parameter is $e = 0.5$. In the investigated temperature range, the integrated ESR intensity, $I_{\text{ESR}}$, displays a Curie behaviour (Fig. 4) in agreement with the theoretical predictions appropriate to quantum size effects of small metal particles [8].

A Curie–like behaviour has previously been reported for ESR in uniform platinum microcrystals having the mean size about 2 nm [9]. The transition from Curie to Pauli behaviour, which is a characteristic feature of the electronic susceptibility in the quantum limit, could unfortunately not be observed since the ESR signal disappears above 60 K.

For the bulk metals the spin relaxation mechanisms is dominated by spin–orbit coupling and the relaxation times are very short. As a result the spectra are too broad to be observed even at low temperatures. When the metal particles are very small, the average electronic energy level spacing, $\delta$, becomes larger than the Zeeman energy $h\nu$. In this case the spin relaxation processes are quenched by quantum size effects, resulting in a narrowing of the CESR line [9].

In accordance with Kawabata’s theory, the ESR linewidth of very small metal particles is given by [4].

$$\delta H_{1/2} \approx \frac{V_F (\Delta g)^2 h \nu_e}{\delta \tau d_m}$$  \hspace{1cm} (1)

where $V_F$ is the Fermi velocity of the conduction electrons, $\Delta g$ is the bulk metal $g$ shift ($\Delta g = g_{\text{bulk}} - g_m$), $h\nu_e$ is the Zeeman energy, $\delta$ is the average electronic energy level spacing of the metal, $\eta$ is the electron magnetogyratic ratio and $d_m$ is the mean metal particle diameter.

Following Kubo, the quantum size effects alter the electronic properties of small metal particles and we have [8]

$$\delta = \frac{2m_r V_F^2}{3n(\pi/6)d_m^3} \quad \text{with} \quad V_F = \frac{h}{2\pi n_e}(3\pi^2 n)^{1/3}$$  \hspace{1cm} (2)

where $n$ is the number of atoms/m$^3$ in a particular metal, $m_r$ is the free electron mass and $\delta$ is inversely proportional to the particle volume. By combining Eq. (2) with Eq. (1) and using the specific parameters for Pt–metal ($\rho = 21.472$ g cm$^{-3}$, $M = 195$ g mol$^{-1}$, $V_F = 14.4905$ m s$^{-1}$), the expression for $\delta H_{1/2}$ turns out to be [10].

$$\delta H_{1/2} = 135 \times 10^2 (\Delta g)^2 d_m^2 (\text{nm}^2) G$$  \hspace{1cm} (3)

The experimental $g$–factor of bulk Pt metal is not known. The corresponding $\Delta g$(Pt) could be estimate from the $\Delta g$–value for silver metal, $\Delta g$(Ag) = $-1.9 \times 10^{-2}$ [10]. Because $\Delta g$ is proportional to $\lambda/\Delta E$, $\lambda$ being the spin–orbit coupling, one could consider that the percentage change in $\Delta g$ is similar to that exhibited by spin orbit coupling in going from Ag($\lambda = - 1769$ cm$^{-1}$) to Pt($\lambda = - 2239$ cm$^{-1}$). Then, one gets

$$\Delta g(Pr) = -1.9 \times 10^{-2} \frac{(2239)}{(-1769)} = -2.4 \times 10^{-2}$$  \hspace{1cm} (4)

Substituting into Eq. (3) the evaluated value for $\Delta g$(Pt), we estimated the mean diameter of Pt-particles within porous Al$_2$O$_3$ channels as $d_m = 6$ nm. The observed difference between the Pt–crystallite mean size, $D_m$, as resulting from X–ray diffraction analysis and $d_m$ evaluated from Kawabata’s theory could be partially due to: (i) the uncertainty in $\Delta g$(Pt) evaluation (ii) the skin-effect which drives electric and magnetic components out of phase in the sample and therefore Pt – particles large compared to the skin–depth may not contribute to the resonance. The presence of the skin–effect is supported by the asymmetry of CESR line ($e > 0$) in Pt/Al$_2$O$_3$ membrane.
4. Conclusions

The CESR spectra of Pt – nanoparticles deposited in the channels of Al$_2$O$_3$ membranes were observed only in a narrow temperature range: 6 - 50 K. The corresponding CESR parameters, g – factor and the linewidth are temperature independent. The ESR integral intensity, which is proportional to the electronic susceptibility, follows a Curie law. It is a characteristic feature of a quantum size effect confirming that the condition $h v_c < \delta$ is satisfied for Pt- metal particles.

From the experimental value of the CESR linewidth and taken into account the Kawabata’s theory, a Pt- particle mean diameter of ≈ 6 nm was derived. Only a fraction of Pt – particles with the size distribution of Fig. 2 (having diameters less than the skin – depth) is contributing to the resonance.

References