The values are very similar which shows the good applicability of the three methods to the system under study.

CONCLUSIONS

1. The harmonic analysis and faradaic rectification methods confirm the conclusions both of the theoretical work (1-3) and the experimental work carried out by other authors for other systems (4).

2. Both techniques have over the a.c. impedance or the polarization resistance the advantage of allowing the determination of the corrosion rate without the knowledge of the Tafel coefficients which are very often difficult to estimate.

3. For the system studied, since it is activation controlled, both methods gave very similar results for the corrosion rate, which are self checked through the use of the Stern-Geary equation.

Similar agreement of results was obtained by Gill et al. (4) for carbon steel in NaCl solution, although as stated by those authors, for more complex systems there is no guarantee of identical success.

REFERENCES

- Devay, J.; Meszaros, L.; Acta Chim. Acad. Sci. Hung., <u>100</u>, 183 (1979)
- 2. Devay, J.; Meszaros, L.; Acta Chim. Acad. Sci. Hung., <u>104</u>, 311 (1980)
- 3. Meszaros, L.; Korrosios Figyelo; 21, 30 (1981)
- 4. Gill, J.S.; Callow, L.H.; Scantlebury, J.D.; Corrosion, <u>39</u>, 61 (1983)

(Accepted, 10 December 1991)

OXYGEN REDUCTION ON PLATINUM ELECTRODES COATED WITH NAFION

C. Paliteiro^{*}, M.L. Pereira and A.M. Jorge Department of Chemistry, University of Coimbra, P-3049 Coimbra, Portugal

ABSTRACTS: The electroreduction of O_2 in 0.5 M H_2SO_4 on platinum finely dispersed on pyrolytic graphite and coated with Nafion films ranging in thickness from 0.5 to 18 μ was studied. It was found that i) the film does not alter the mechanism of the reduction reaction; ii) the film does not prevent sintering of the catalyst; iii) the film concentrates O_2 from the solution but, nevertheless, the current measured for the filmed electrodes only increases relatively to the uncoated electrodes near the onset of the reduction when electron transfer controls; once diffusion becomes important the current decreases because, whatever the thickness, the transport of O_2 inside the film is slowed down; iv) thick films behave like recast films whereas thin films behave like membranes.

1. INTRODUCTION

In gas phase and at low temperatures O_2 adsorbs dissociatively on platinum so that at 150 ⁰K there are O atoms on the surface [1]. In solution, however, O_2 has to compete with water or with specifically adsorbed ions (electrolyte anions for example) for the Pt surface and therefore its interaction with this surface is only favoured at the pzc. On the other hand, Pt is used finely dispersed in practical porous electrodes in order to obtain high current densities; however, due to the gradual sintering of the Pt particles these practical electrodes cannot sustain such high currents for a long time.

In this context, there has been considerable interest in the incorporation of perfluorosulphonic acids like Nafion Into O_2 cathodes. With the use of these ionomers it is hoped: a) to take advantage of the lower dielectric constant in the ionomer phase to favour O_2 adsorption on catalytic sites thus decreasing the reduction overpotential; b) to take advantage of increased O_2 concentration inside the ionomer phase next to the electrode to increase the current at a given overpotential; c) to decrease the loss of the surface area of the catalyst by slowing down processes possibly responsible for that loss, such as surface detachment of the catalyst particles from the carbon suport and classical "Ostwald ripening"; d) to take advantage of the catalyst surface by the electrolyte anions.

Portugaliæ Electrochimica Acta, 9 (1991) 507-523

This paper reports a study of the influence of Nafion on the activity of platinum dispersed on graphite for the electroreduction of O_2 in 0.5 M H₂SO₄. The reduction of O_2 on bulk platinum coated with a Nafion film of $\approx 26 \mu$ (wet film) was first studied by the group of Srinivasan [2]. We examined a wide range of Nafion thicknesses and the dispersed form of the catalyst we worked with is closer to that used in a practical electrode.

2. EXPERIMENTAL

Before the deposition of Pt, the PGb disc was first polished with 0.1 μ diamond paste on a microcloth and cleaned afterwards with ethanol and pyrolysed water in a ultrasonic bath.

Platinum was deposited on a pyrolytic graphite disc formed into a rotating disc electrode and exposing the basal surface (PGb) following a method developed by G. Troughton [3] by which the PGb surface is kept at 80 °C for 1 h in contact with a stirred solution of 10^{-3} M PtCl₆²⁻ at pH 3 before the pH is adjusted at pH 7 and Pt is deposited using formaldehyde as the reducing agent. When applied to the preparation of porous electrodes, this method gives rise to a uniform dispersion of well adherent particles with size ranging from 2 to 50 nm but predominantly of 2 nm [3]. Optical examination of our films also revealed a uniform coverage of the PGb disc by Pt. This first layer of well adherent Pt may be covered by a thin film of very small Pt particles, which apparently interact only physically with the second layer. The real exposed Pt area (as determined from the charge needed to adsorb one monolayer of $\rm H_2$ from 0.5 M $\rm H_2SO_4$ under argon saturation [4]) was found to be 3 to 4 times the geometric area for the first layer and about 14 times the geometric area when the second layer forms. In this case, however, the decrease of the electroactive area of Pt is inicially fast and then follows the pattern described in the results section below for the first layer; the adherence of the second layer is therefore very poor. Giving the PGb disc a 0.1 µ finish with diamond paste before Pt deposition reproducibly leads only to the first layer; an increase in the graphite roughness apparently favours the formation of the second layer. The results presented and discussed below relate to "first-layer" deposits of Pt.

After deposition the PG+Pt disc was carefully washed with pyrolysed water and left overnight also in pyrolysed water to remove any residual formaldheyde.

The Nafion coatings with thickness ≥ 9 µ in Tables 1 and 2 were prepared by droping on the PGb+Pt disc from a microsyringe an adequate volume of a 3 % (w/v) solution of Nafion 117 in water and ethanol and allowing the solvent to evaporate in a oven at 80 °C. The films of about 0.5 μ studied were prepared as above from a 1 % (w/v) solution obtained by dilution of the 3 % solution. The dilution was done either by adding ethanol (films 2 and 3) or a 1:1 mixture of water and ethanol (film 1). The films thus obtained were washed with pyrolysed water and left overnight also in pyrolysed water to remove any residual organic impurity. Since we were not able to measure the film thickness, this was calculated assuming that films had cllindrical geometry and taking the density of wet Nafion films (1.58 [57]) as the value of film density. The values of the concentration of the Nafion solutions used in the calculation were obtained by measuring a certain amount of the solution, evaporating the solvent to dryness and weighting the Nafion deposited.

Experiments were performed using a potentiostat, a X-Y recorder and a rotator and its controller supplied, respectively, by Pine Instruments, Philips and Oxford Electrodes. The electrochemical cell was termostated at 25 °C. Potentials were measured against a standard calomel electrode but hereafter they are referred to the reversible hydrogen electrode (RHE). The counter electrode (a glassy carbon rod) was separated from the working electrode compartment by a fine glass frit. Argon (type N46, 99.995%) and oxygen (type C, > 99.5 %) were supplied by Air Liquide.

3. RESULTS

a) The PGb + Pt electrode.

The cyclic voltammogram (CV) of PGb+Pt is identical to the CV of bulk polycrystalline Pt (polyc Pt) (see Fig. 1 c)); the small intensity of the desorption peak of strongly-adsorbed hydrogen atoms is an indication that very small Pt particles are present on the surface [6].



Fig. 1: Cyclic voltammograms recorded at 50 mV s⁻¹ on a PGb+Pt electrode in argon-saturated 0.5 M H_2SO_4 : a) first scan after Pt deposition; b) first scan after recording the polarization curve of Fig. 5a); c) steady-state after 1h 15 min scanning; current intensity scale: 50 μ cm⁻¹ for (a) and (b) and 20 μ cm⁻¹ for (c).

However, the first CV recorded after Pt deposition is always like that shown in Fig. 1 a). Such a CV is not related to a Pt surface blocked for example with formaldehyde residues. More probably, instead, Pt particles deposit exposing the (111) surface. We checked that with the following experiment: immediately after the CV of Fig. 1a) was recorded, the electrolyte was saturated with O_2 keeping the electrode at the rest potential; the polarization curve of Fig. 2a) was then recorded under O_2 saturation. The small hysteresis of the cathodic and the anodic curves and its crossing at about 600 mV indicate an electrode free from organic impurities [2]; a blocked surface gives polarization curves where the anodic and cathodic scans have a much higher hystheresis and cross at a more positive potential and where the current is generally decreased relatively to a unblocked surface (cf. Fig. 2b)). The electrolyte was then deoxygenated while the electrode was kept at the rest potential and the CV of Fig. 1b) was recorded under argon saturation. After 1 h 15 min of potential cycling the CV of Fig. 1c) was obtained. In Fig. 1, CV (b) shows some differences from CV (a) towards the CV of dispersed polycrystalline Pt (cf CV (c)) but it still is featureless in the hydrogen adsorption/desorption region. It is therefore probable that the method of Pt deposition used gives rise to Pt particles oriented so that they expose only (111) planes. Upon cycling, i) the (111) surface probably facets so that the CV features characteristic of other exposed low-index planes [7] develop with time and the CV of polycrystalline Pt is finally obtained; ii) loosely-attached particles fall off leading to a decrease of the real area. This decrease in area goes on slowly even if the electrode is kept in pyrolysed water, which may indicate either that sintering is occurring or that diffusion of Pt atoms along the surface of the larger particles gives them a more spherical shape.





- 511 -

Fig. 3 a) shows polarization curves for O_2 reduction on PGb+Pt. They have two well defined Tafel regions; the Tafel slope is 50-60 mV dec⁻¹ at low overpotential (η) and 200-220 mV dec⁻¹ at high η . Therefore at low n PGb+Pt approaches the behaviour of polyc Pt in the same solution, suggesting the ocurrence in both cases of the same reduction mechanism. However, at high n the Tafel slope for PGb+Pt is significantly higher than 120 mV dec⁻¹, the slope usually observed with polyc Pt in the same potential range [8]. This increase of the Tafel slope at high n is probably explained by the very slow reduction of O_2 on the graphite substrate that becomes also possible in this overpotential region.



Fig. 3: Polarization curves recorded at 10 mV s⁻¹ for O₂ reduction in O₂-saturated 0.5 M H₂SO₄ on a a) (----) PGb+Pt electrode and a b) (...) PGb+Pt+ 0.44 μ Naf electrode.

A linear Levich plot (cf. Fig. 4a)) indicates that the current is diffusion-controlled. The Koutecky-Levich plots (Fig. 5) are also linear with slopes that correspond to a 4-electron reduction; at low current densities apparent number of electrons between 5 and 6 were found indicating H_2O_2 disproportionation [9].





- 513 -



- 514 -

b) The PGb+Pt+Naf electrode.

The first CV of PGb+Pt+Naf recorded was similar to the first CV of PGb+Pt. Continuous scanning between 20 and 1300 mV gradually restores the CV of the steady-state PGb+Pt surface (see Fig. 6) but the electrochemically active area of Pt decreases. The observed decrease was 30 to 40% of the initial Pt active area whatever the film thickness studied.

Typical polarization curves obtained on PGb+Pt+Naf electrodes are shown in Fig. 3b). We found that: i) Nafion coatings decrease the reduction current in all but the very begining of the polarization curves. ii) Two Tafel regions are also obtained and the Tafel slopes agree well with those found with uncoated electrodes. iii) The Koutecky-Levich plots are linear (see Fig 5b)) and have the same slope as that found for PGb+Pt at the same potential; iv) The Levich plot curves down relatively to the same plot for PGb+Pt; this negative deviation increases as the Nafion thickness increases (see Fig. 4, (b) to (e)). Therefore, the presence of a Nafion film do not seem to affect the mechanism of O_2 reduction on PGb+Pt but, in most of the potential region where O_2 is reduced, the film decreases the reduction rate.



Fig. 6: CV recorded at 50 mV s⁻¹ with electrodes of a) PGb+Pt and b) PGb+Pt+0.44 μ Naf in a argon-saturated 0.5 M H_2SO_4 solution.

4. FURTHER ANALYSIS OF RESULTS

The PGb+Pt+Naf electrode is a RDE coated with a film without redox activity. In this case the limiting current I_{L.f} is given by *[10]*

 $I_{L,f} = I_{L} \left[1 / (1 + P_{s} / P_{f}) \right]$ (1) where I_{L} is the limiting current for PGb+Pt, $P_{s} = D / x_{d}$ is the solution permeability for O_{2} and $P_{f} = \beta D_{f} / d_{f}$ is the film permeability for O_{2} .

- 515 -

It is easily seen that equation 1 describes the general shape of the Levich plots in Fig. 3 (b) to (e). D and x_d are, respectively, the diffusion coefficient of O_2 in the solution and the thickness of the RDE diffusion layer; P_s is therefore the rate constant for O_2 transport in solution. β , D_f and d_f are, respectively, the partition coefficient of O_2 between the film and the solution, the diffusion coefficient in the film and the thickness of the film. P_f expresses therefore the combined effects on $I_{L,f}$ of the O_2 exchange between the solution and the Mafion film and the rate constant for the transport of O_2 in the film.



Fig. 7: Levich Plot. The points were obtained from the polarization curves for a PGb+Pt+13 μ Naf; the curve was fitted to the experimental points as described in text.

It is then possible to calculate P_f , C_f and D_f for a given film by the following method:

a) Equation 1 can be written in the form:

 $y = A_1 P_f x / (P_f + A_2 x)$ (2) where $A_1 = 0.62 n F A D^{2/3} v^{-1/6} C$ and $A_2 = 0.62 D^{2/3} v^{-1/6} are$ constants, $y = I_{L,f}$ and $x = \omega^{0.5}$; n is the number of electrons per reduced O_2 molecule. A is the geometric electrode area, ϑ is the kinematic viscosity and C is the solution concentration of O_2 . Therefore P_f can be calculated as the numeric value that fits equation 2 to each of the Levich plots of Fig. 3 (b) to (e). An example of such fitting is given in Fig. 7.

b) Once P_f is known, from P_f = C_f D_f / C d_f it is possible to calculate the product C_f D_f .



Fig. 8: Linear sweep voltammograms recorded with a PGb+Pt+ +18 μ Naf electrode in 0.5 M H_2SO_4 saturated with a) (----) O_2; b) (...) argon.

c) The application of linear sweep voltammetry to the PGb+Pt+Naf electrode under O₂ saturation provides a scan-rate dependent peak current I_p (see Fig. 8), which, after correction for the current measured under argon at the peak potential, is given by [11]:

$$I_p = 2.99 \times 10^5 \text{ n } a^{0.5} \text{ A } D_f^{0.5} C_f v^{0.5}$$

where a is the transfer coefficient calculated from the Tafel slope

at high η and v is the scan rate. As I_p varies linearly with $v^{0.5}$ (see Fig. 9), $D^{0.5}$ C_f can be calculated from the line slope. Since the product D_f C_f was previously calculated, D_f and C_f can be individually determined.



Fig. 9: I_p ($\omega^{0.5}$) plot obtained from the voltammograms in Fig. 8

Table 2 summarizes the results obtained; X is the slope of the $I_p(v^{0.5})$ line and in the calculations we made D = 1.77 x 10^{-5} cm² s⁻¹ [12], $v = 9.79 \times 10^{-3}$ cm² s⁻¹ [12], C = 1.1 x 10^{-6} mol cm⁻³ [12] and n = 4. Table 1 contains information on the areas of the different surfaces studied.

4. DISCUSSION

Before a discussion of the above-mentioned results is made the following question has to be asked: to what extent is the morphology of a Pt deposit and of a Nafion film affected by the electrochemical experiments carried on those deposits and on those films? To answer this question we examined PGb+Pt and PGb+Pt+Naf electrodes by optical microscopy before and after voltammetric experiments on them. The method of Pt deposition applied produced deposits that covered uniformly the PGb disc and it was impossible to individualize the Pt particles with the magnification applied (200 x). As a consequence of the experiments some of these particles detach from the disc or dissolve so that the area of the PGb substrate directly exposed to the electrolyte gradually increases with time. This fact explains the observed decrease in the active area of PGb+Pt electrodes and also the increase of the Tafel slope at high n for O_2 reduction on those electrodes relatively to the Tafel slope observed for the same reaction on bulk Pt.



Fig. 10: CV recorded at 50 mV s⁻¹ in a argon-saturated 10^{-3} M Fe(CN)₆⁴⁻ + 0.1 M KCl solution with a a) (----) PGb electrode; b) (...) PGb+Naf electrode.

We also observed that, although initially smooth and uniform, the surface of the Nafion films became furrowed after the voltammetric experiments carried on them. However, the furrows were only superficial since, even when they were present, there was no contact between the electrolyte and the substract surface underneath the film. This was checked as described next following the method suggested by Bard and coworkers [13]. The CV recorded for the PGb surface in a

- 519 -

 10^{-3} M ${\rm K_4Fe(CN)_6}$ + 0.1 M KCI solution showed the expected peaks correspondent to the ${\rm Fe(CN)_6}^{4-}$ / ${\rm Fe(CN)_6}^{3-}$ couple (see Fig 10a)) whereas the CV recorded for a PGb+Naf electrode was practically identical to the CV of PGb in 0.1 M KCI (see Fig 10b)). This was observed for all the thicknesses studied (0.5, 5 and 10 μ) both with smooth and furrowed films. As a Nafion film is permselective to cations, the absence of the peaks relative to the ${\rm Fe(CN)_6}^{4-}$ / ${\rm Fe(CN)_6}^{3-}$ couple in the CV for the PGb + Naf electrode means that the electrolyte does not directly contact the PGb surface underneath the film.

However, the fact that the CVs for PGb+Pt and PGb+Pt+Naf electrodes have the same shape (cf. Fig. 6) shows that the electrolyte can permeate through the film. On the other hand and as mentioned above, in the presence of a Nafion film the active area of Pt reduces to 60 to 70% of the initial active area whatever the film thickness. This fact probably means that i) 30 to 40 % of the PGb+Pt surface is used to anchor the film whatever the thickness and ii) the film anchors by the hydrophobic region [14] of its microstructure.

Now we can discuss the results summarized in Tables 1 and 2; we will distinguish between high and low film thickness.

TABLE 1

Film	df	Ageom	A _{Pt}	A _{Naf}	A _{Pt} /A _{geo.}	A _{Pt} /A _{Naf}
numb.	(μ)	(cm ²)	(cm ²)	(cm ²)		(%)
1	0.43	0.440	1.2	0.7	2.7	58
2	0.44	0.420	1.1	0.8	2.6	73
3	0.56	0.400	1.2	0.7	2.8	58
4	9/initial	0.465	1.3	1.0	2.8	78
5	9/+6 days	0.465	-	0.9	-	-
6	13	0.450	1.6	1.0	3.6	63
7	18	0.465	-	0.7	-	-

1001000 00 3

TABLE 2

Film	df	Pf	Х	°f	β	Df
number	(µ)	(cm s ⁻¹)	(As ^{0.5} v ^{-0.5})	(cm s ⁻¹)		(cm ² s ⁻¹)
		(x 10 ²)	(x 10 ³)	(x 10 ⁵)		(x 10 ⁶)
1	0.43	5.3	1.66	1.7	15.5	0.15
2	0.44	6.1	1.65	1.5	13.6	0.20
3	0.56	6.2	1.55	1.1	10.0	0.28
4	9/ini	0.86	2.1	0.65	5.9	1.3
5	9/+6d	0.92	2.0	0.57	5.2	1.5
6	13	0.62	2.0	0.54	5.0	1.6
7	18	0.48	2.1	0.58	5.3	1.6

a) Results at high film thickness (films 4 to 7).

 P_f decreases as d_f increases as expected from the equation $P_f = \beta D_f / d_f$ (cf. Table 2). On the other hand D_f and β are practically independent from d_f . This means that the rate constant for the transport of O_2 in the Nafion film, K_D , $f = D_f / d_f$, decreases as d_f increases. Therefore, wherever diffusion is significant in the polarization curve (i.e. in the mixed-control and in the limiting-current regions), the presence of Nafion decreases the current.

 C_f is greater than C by a factor of 6 and is independent from d_f in this thickness range. However, this increased concentration of O_2 only shows in the region of the polarization curve where the current is entirely controlled by electron transfer.

The values of C_f and D_f found in this d_f range compare well with those found by Srinivasan and coworkers for a 22 μ - thick <u>recast</u> film of Nafion on polyc Pt [2].

The active area of Pt in PGb+Pt+Naf electrodes decreases with time while P_f increases even if the electrode is kept in pyrolysed water (cf. Table 1, films 4 and 5). Therefore the sintering of the Pt particles is not prevented by the presence of a Nafion film with the chemical and physical characteristics of a recast film. The increase of P_f with time is probably due to water absorption.

b) Results at low film thickness (films 1 to 3).

Relatively to the films of higher thickness, an analysis of the data of Table 2 for films 1 to 3 shows that i) as expected the permeability of Nafion films about 0.5 μ -thick is much higher, ii) D_f is one order of magnitude lower and iii) C_f is 2 to 3 times greater. Since a low value of D_f is normally related to a film with a microstructure of low water content [15] and O₂ is five times more soluble in the hydrophobic region than in the ionic cluster region [16], it appears that, relatively to the high-thickness films, in the Nafion films of low thickness the proportion of the hydrophobic region increases and the water content consequently decreases. In fact, the values of D_f and C_f for the films of about 0.5 μ studied in this work (specially for film 1 which was deposited more slowly) are characteristic of a Nafion *membrane* [17] and not of a recast film.

From the values of $P_f = D_f / d_f$ the values of the rate constant for the transport of O_2 in the film, $K_{D,f} = D_f / d_f$ can be calculated. We found 3.5×10^{-3} , 4.5×10^{-3} and 6.3×10^{-3} cm s⁻¹, respectively, for films 1, 2 and 3. These values of $K_{D,f}$ are only 3 to 5 times higher than those found for the thicker films. For rotation rates up to 9 s⁻¹, they also are of the same order of magnitude of the rate constant K_D for the transport of O_2 in the solution. At 9 s⁻¹ K_D becomes greater than $K_{D,f}$ and, above that, the higher the rotation rate the higher the separation between the two rate constants.

The transport of O_2 is then limited even by a Nafion film of 0.5 μ . Therefore, the prediction advanced by the group of Srinivasan that a Nafion film would not pose an O_2 transport problem in 0.5 M H_2SO_4 if thinner than 4 μ [2] does not hold, probably because thinner films behave like membranes and not like well hydrated recast films as the group assumed.

To conclude, we can say that the data collected in this work demonstrate that the application of Nafion-coated Pt electrodes to the electroreduction of O_2 will only be useful if the structure of Nafion is modified so that O_2 diffusion through the film is increased; besides, Pt particles have to be coated in such a way that sintering is prevented.

ACKNOWLEDGMENTS

We gratefully thank Professor Andrew Hamnett for the gift of the Nafion solution and for helpful discussions.

REFERENCES

- 1. J.M. Heras and L. Viscido, Cat. Rev. Sci. Eng., 30 (1988) 31.
- S. Gottesfeld, I.R. Raistrick and S. Srinivasan, J. Electrochem. Soc., 135 (1987) 1455.
- 3. G. Troughton, MSc Thesis, University of Oxford, 1989.
- 4. R. Woods, *Electroanal. Chem.*, Ed. A.J. Bard, Marcel Dekker, N.Y., 9 (1976) 1.
- 5. D.R. Lawson, L.D. Whiteley and C.R. Martin, J. Electrochem. Soc., 135 (1988) 1455.
- K. Kinoshita, J. Lundquist and P. Stonehart, J. Catal., 31 (1973) 325.
- K. Yamamoto, D.M. Kolb, R. Kotz and G. Lehmpfuhl, J. Electroanal. Chem., 96 (1979) 233.
- 8. D.B. Sepa, V. Vojnovic and A. Damjanovic, *Electrochim. Acta*, 26 (1981) 781.
- 9. C. Paliteiro, Lectures of the IX Iberoamerican Congress on Electrochemistry, Ed: University of La Laguna, Tenerife, Spain, 1990, 331.
- 10. D.A. Gough and J.K. Leypoldt, Anal. Chem., 54 (1979) 439.
- 11. R.S. Nicholson and I. Shain, Anal. Chem., 36 (1964) 706.
- 12. H. Bala, Z. Phys. Chem., Neue Folge, Bd. 141, S. 91 (1984) 91.
- M. Krishnan, X. Zhang and A. Bard, J. Am. Chem. Soc., 106 (1984) 7371.
- K.A. Mauritz and A.J. Hopfinger, Mod. Asp. Electrochem., 14 (1985) 425.
- 15. A. Parthasarathy, C. Martin and S. Srinivasan, J. Am. Chem. Soc., 106 (1991) 916.
- 16. C. Lee and M.A.J. Rodgers, J. Phys. Chem., 88 (1984) 4385.
- 17. Z. Ogumi, T. Kuroe and Z. Takehara, J. Electrochem. Soc., 132 (1979) 2601.

(Received 30 December 1991)