JOURNAL OF APPLIED ELECTROCHEMISTRY **23** (1993) 1107–1116

A.c.-impedance spectroscopy study of oxygen reduction at Nafion® coated gas-diffusion electrodes in sulphuric acid: Teflon loading and methanol cross-over effects

A. S. ARICÒ, V. ANTONUCCI, V. ALDERUCCI, E. MODICA, N. GIORDANO

CNR Institute for Transformation and Storage of Energy, Salita S. Lucia sopra Contesse 39, S. Lucia, Messina, Italy

Received 30 November 1992; revised 1 April 1993

The kinetics of oxygen reduction have been studied at Nafion®-coated dual layer gas-diffusion electrodes at 60 °C in 2.5 M H_2SO_4. A.c. impedance and steady state galvanostatic measurements have been carried out on electrodes containing various PTFE loadings. A.c. impedance spectroscopy supplied information on charge transfer resistance, series resistance and double layer capacitance of electrodes during the oxygen reduction process. These parameters, together with those derived by d.c. measurements (i.e. Tafel slopes, charge transfer coefficient, etc.), allowed a better identification of the features governing the electrode efficiency and the reduction mechanism. The best electrode was found to be one containing 30% PTFE; this showed both the lowest charge transfer resistance and the lowest overpotential for oxygen reduction. This electrode also showed lower overpotential than the same uncoated electrode at low current densities. The poisoning effect by methanol has been also investigated. Upon addition of methanol to the solution, no change was observed in the reaction mechanism at low overpotentials. In contrast, a significant variation of the Tafel slope was observed at high overpotentials. This behaviour is interpreted in terms of the variation of Pt–O bond strength as a function of electrode potential.

1. Introduction

The kinetics of oxygen reduction on platinum at solid polymer electrolyte interfaces has been extensively investigated in recent years [1–5] to improve the efficiency of fuel cells operating at low temperature [6, 7]. Polyperfluorosulphonic acid hydrated polymers such as Nafion® are mainly used as electrolytes in low temperature fuel cell systems. The achievement of high efficiencies for the oxygen reduction reaction with electrodes containing low platinum loadings has been made possible incorporating a Nafion® gel within the platinized carbon and the PTFE binder. Nafion® gel enables the porous carbon to be integrated to the electrolye by producing an extension of the three-dimensional reaction zone [6].

Use of Nafion® membranes is gaining momentum in H_2–O_2 SPEFCs and in low temperature direct methanol fuel cells (DMFCs) due to their high proton activity, low ionic resistance and preparation as a thin electrolyte layer. DMFCs operating with liquid fuel require a methanol-containing anolyte with suitable water and protonic activity contents. These requirements are satisfied by sulphuric acid at concentrations equal to or less than 2.5 M [8]. The excellent oxygen solubility and diffusivity of perfluorosulphonated ionomers [1, 2, 9] together with minimal anion adsorption on electrodes observed for fluorinated acids [10], produce favourable conditions for the oxygen reduction kinetics.

Perfluorosulphonated ionomers are cation permselective, hence they may produce a reduction of the sulphate anion adsorption at the cathode, but they partially block the platinum sites. The Nafion® gel represents a suitable coating for the cathode in the presence of the sulphuric acid electrolyte since it is only slightly soluble in this medium. Several investigations carried out on bare electrodes have been conducted to determine if Nafion® protects the platinum surface against the adsorption of phosphate anions in phosphoric acid solutions [2]. It has been observed that Nafion® filmed electrodes are probably permeable to neutral H_3PO_4 molecules that dissociate near the platinum surface [2], but, at low overpotentials, an increase in the oxygen reduction reaction (ORR) was found for Nafion® filmed bare platinum electrodes, equilibrated with diluted sulphuric or phosphoric acid [2].

Gas-diffusion electrodes containing Nafion® coatings show different oxygen diffusivity and film adherence characteristics relative to bare electrodes. In the gas-diffusion electrodes, oxygen is supplied at the catalyst particles through hydrophobic polytetrafluoroethylene channels. The present study is devoted to the investigation of oxygen reduction kinetics at Nafion® coated gas-diffusion electrodes. The electrodes, containing various PTFE amounts, were tested in

0021-891X © 1993 Chapman & Hall

sulphuric acid electrolyte and in the presence of dissolved methanol. The solution concentration and temperature were typical of those in a DMFC.

Both galvanostatic steady-state polarization and electrochemical a.c.-impedance spectroscopy (EIS) techniques were used. EIS supplies information that cannot be easily obtained by d.c. techniques, especially in the case of coated electrodes. The kinetic parameters, derived from galvanostatic experiments (i.e. Tafel slope, charge transfer coefficient and number of electrons involved in the rate determining step), are thus complemented by series resistance, double layer capacitance and charge transfer resistance values obtained from a.c.-impedance spectroscopy. It is thus possible to gain more information on the factors controlling the oxygen reduction at the Nafion® film coated electrodes. Although dual-layer gas-diffusion electrodes (i.e. electrodes composed of a catalytic layer deposited onto a wet proofed carbon paper acting as a gas diffusion layer) have been chosen for the present investigation, information obtained in such conditions can also be useful for electrodes of different morphologies.

2. Experimental details

The carbon supported platinum catalyst used in the preparation of the gas-diffusion electrodes was from Johnson Matthey (10% Pt/C). The electrodes were prepared from carbon paper (Toray TGP 90) wetproofed with a solution of fluoroethylene propylene polymer (FEP T 120, DuPont), dried at 70 °C, and sintered at 340 °C for 15 min; the final FEP loading was 5 mg cm^{-2}. The catalyst paste was obtained by mixing under continuous stirring, in a thermostated ultrasonic bath (60 °C, 30 min), the catalyst powder with an appropriate amount of PTFE dispersion (61% Teflon 30 N DuPont) followed by isopropyl alcohol addition at room temperature. The flocculate was spread by a doctor-blade technique onto the carbon paper. The electrodes were dried in air at 120 °C for 1 h, followed by thermal treatment at 280 °C for 30 min, and finally sintered in air at 340 °C for 30 min. Gas-diffusion electrodes containing catalytic layers with 0.5 and 0.25 mg Pt cm^{-2} were prepared by this procedure. Electrodes were impregnated with Nafion® in order to obtain a film of the proton conductor inside the catalyst layer. The impregnating solution contained a 5% w/w Nafion® 1100 EW solution (Solution Technology Inc.) and isopropyl alcohol (85% isopropanol and 15% H_2O). The Nafion solution was deposited onto the active layer of the electrode using a graduated pipette. The impregnated electrodes were dried at room temperature for 15 h and then heat treated for 1 h at 130 °C under vacuum. The Nafion® loading was proportional to the volume of the deposited solution and was maintained constant at about 0.3 mg Nafion® per mg Pt/C catalyst powder.

The electrochemical measurements were carried out in a conventional three-electrode cell containing 2.5 M H_2SO_4 electrolyte. The gas-diffusion electrode was mounted into a Teflon holder containing a platinum ring current collector and having provision for feeding oxygen gas (1 atm, 200 cm^3 min^{-1}). The electrode area exposed to the electrolyte was 1.5 cm^2. A large area platinum gauze was used as counter electrode. A saturated calomel reference electrode was placed externally to the cell and connected to the main compartment through a Luggin capillary whose tip was placed close to the working electrode surface. The potential values are reported with reference to the normal hydrogen electrode (NHE). The electrochemical cell had an external jacket through which a solution of ethylene glycol and water maintained at 60 °C by a Haake model F3 thermostat was circulated. The electrochemical cell was connected to an EG&G PAR model 273 potentiostat/galvanostat, a Philips model PM3375 storage oscilloscope and a Solartron 1255 frequency response analyser (FRA), interfaced to an IBM PC via a National Instruments IEEE-488 GPIB card. The amplitude of the a.c.voltage was 10 mV in each case. The EG&G M388 electrochemical impedance software was used to drive and collect the impedance measurements between 100 kHz and 10 mHz. Steady-state galvanostatic measurements for the oxygen reduction process were performed at the various electrodes.

3. Results and discussion

3.1. *Galvanostatic steady-state measurements*

According to the previous studies on oxygen reduction reaction at Nafion® coated electrodes, an optimum Nafion® loading giving the maximum electrochemical activity has been identified. This loading varies according to the electrode morphology. Srinivasan and coworkers [6] have determined an optimum Nafion® loading, in PEM fuel cells, of 0.6 mg cm^{-2} for Prototech electrodes having 0.4 mg Pt cm^{-2} (20 wt % Pt/C) corresponding to about 0.3 mg Nafion® per mg Pt/C catalyst. These authors have indicated ohmic control as a determining feature for electrodes with thinner coatings and diffusion limitations in electrodes with thicker coatings. In previous work carried out in our laboratory, an optimum Nafion® loading of about 0.36 mg Nafion® per mg Pt/C catalyst was determined for the minimization of the cathodic and anodic overpotential in dual layer electrodes for SPE® fuel cells [11]. This loading was found to correspond to a minimum in the ionic resistance.

In the present work attention has been focused on the role of PTFE and methanol cross-over effects for the oxygen reduction reaction at dual layer electrodes, having 0.3 mg Nafion® loading per mg Pt/C catalyst. The aim of the present study was to investigate the conditions corresponding to favourable oxygen reduction kinetics and also to determine if Nafion® provides a suitable barrier to cathode poisoning by methanol in sulphuric acid.

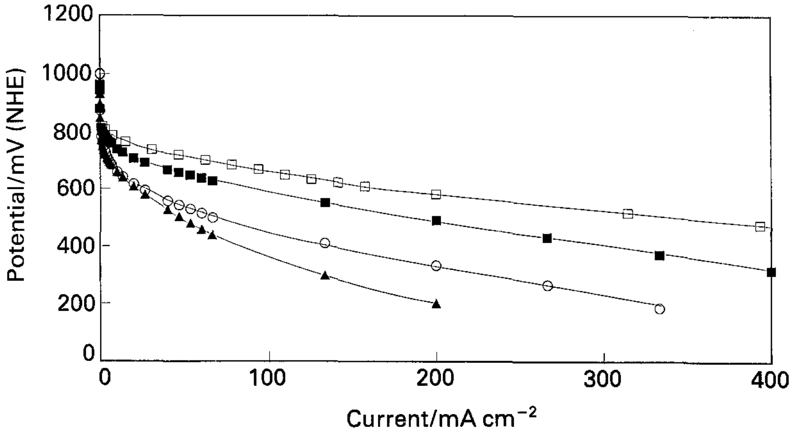

Fig. 1. Galvanostatic steady-state polarization curves for the oxygen reduction at 60 °C on Nafion® coated Pt/C electrodes (0.5 mg Pt cm^{-2}) containing different PTFE amounts. Legend: (■) 20%; (□) 30%; (○) 40%; (▲) 60%.

The galvanostatic steady-state polarization curves for oxygen reduction at 60 °C, on Pt/C electrodes (0.5 mg Pt cm^{-2}) containing various PTFE loadings are shown in Fig. 1. Open circuit potentials are typically above 0.95 V vs NHE; the oxygen reduction is kinetic limited up to about 0.7–0.8 V vs NHE. At more cathodic potentials, the process is ohmic and mass transfer controlled. The electrode containing 30% PTFE shows the lowest overpotentials followed by 20%, 40% and 60% PTFE containing electrodes.

The variation of the oxygen reduction overpotential at different current densities as a function of PTFE loading, is shown in Fig. 2. The maximum activity occurs for the 30% PTFE electrode, both in the kinetic and ohmic-mass transfer limited regions. For Nafion® coated electrodes equilibrated with 2.5 M H_2SO_4, an enhanced activity is found for the electrode containing 20% PTFE with respect to that with 40% PTFE. This behaviour probably derives from better platinum utilization in the 20% PTFE electrode. The resistance is significantly larger in the electrode containing 40% and 60% PTFE. High activity for oxygen reduction has been recently shown by dual layer electrodes with low PTFE loading (11%) [12]. In the dual layer electrodes, the back layer hydrophobic agent significantly influences the value of the PTFE loading at which the maximum activity toward oxygen reduction is recorded.

The maximum activity for oxygen reduction observed for 30% PTFE electrode is in agreement with results obtained for uncoated gas-diffusion electrodes in 20% H_2SO_4 [13, 14]. Similar results have been also obtained in other electrolytes e.g. 7 M KOH and 105% H_3PO_4 [13–15]. Yet, the peculiar result of the present investigation is the large decrease of activity with the increase of PTFE content beyond 30%. This finding may be attributed to the effect of the Nafion® coating. By increasing the PTFE content beyond 30%, the enhanced gas diffusion is counteracted by both the effects of PTFE and Nafion® hydrophobicity which reduce the available platinum sites in contact with H$^+$ ions. The anchoring effect

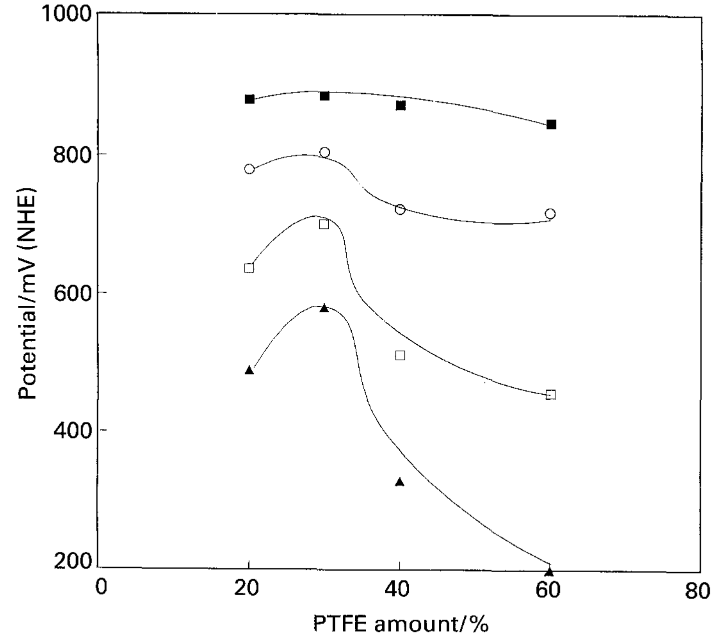

Fig. 2. Variation of the electrode potential for the oxygen reduction as a function of the PTFE content, at different loading currents. Legend: (■), 67 μA cm^{-2}, (○) 3.2; (□) 60; (▲) 200 mA cm^{-2}.

Table 1. Kinetic parameters for the oxygen reduction reaction on Pt/C electrocatalysts in sulphuric acid

Electrode	*Pt loading/ mg cm*$^{-2}$	*Nafion® loading/ mg (mg catalyst)*	*PTFE loading*	*1st Tafel slope*	*2nd Tafel slope*	$(n\beta)_1$	$(n\beta)_2$
a	0.5	0.3	20	-66	−119	1.0	0.55
b	0.5	0.3	30	−62	−131	1.06	0.50
c	0.5	0.3	40	−73	−121	0.9	0.54
d	0.5	0.3	60	−62	−119	1.06	0.55
e	0.25	–	30	−62	−127	1.06	0.52
f	0.25	0.3	30	−70	−137	0.94	0.48
g*	0.25	0.3	30	−64	−172	0.97	0.38

*Tested in 0.5 M CH_3OH, 2.5 M sulphuric acid solution.

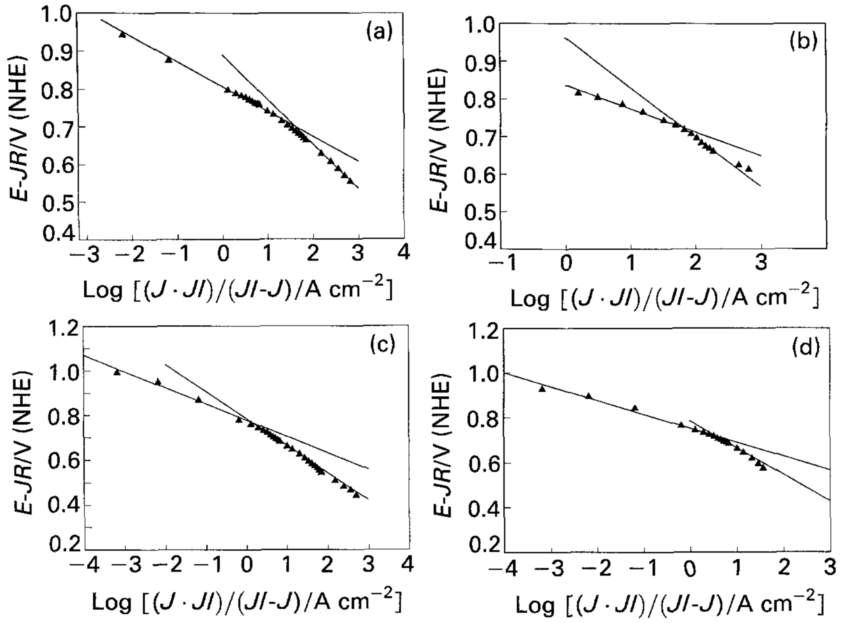

Fig. 3. Tafel plots for oxygen reduction at Nafion® coated Pt/C electrodes containing various PTFE loadings: (a) 20%; (b) 30%; (c) 40%; (d) 60%.

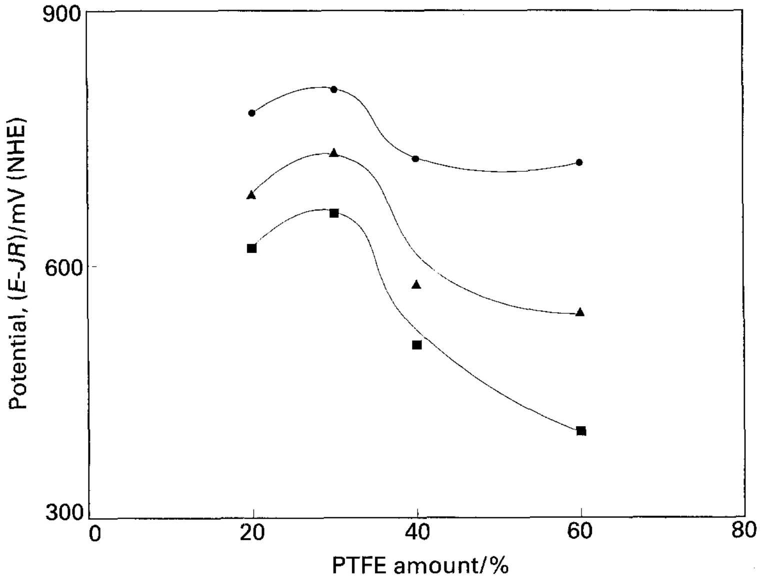

Fig. 4. Variation of the electrode potential in the ohmic drop and mass transfer corrected polarization curves for oxygen reduction at Nafion®-Pt/C gas-diffusion electrodes (0.5 mg Pt cm^{-2}) as a function of PTFE loading. $I \cdot Il/Il - I$: (●) 3.2; (▲) 50; (■) 200 mA cm^{-2}.

by platinum sites of the hydrophobic fluorocarbon structure of Nafion® has been described in the literature [1].

Mass transfer and ohmic drop corrected Tafel curves for oxygen reduction on Pt/C electrodes (0.5 mg Pt cm^{-2}) containing various PTFE loadings, are shown in Fig. 3(a–d); the kinetic parameters deriving from these curves are reported in Table 1. Two

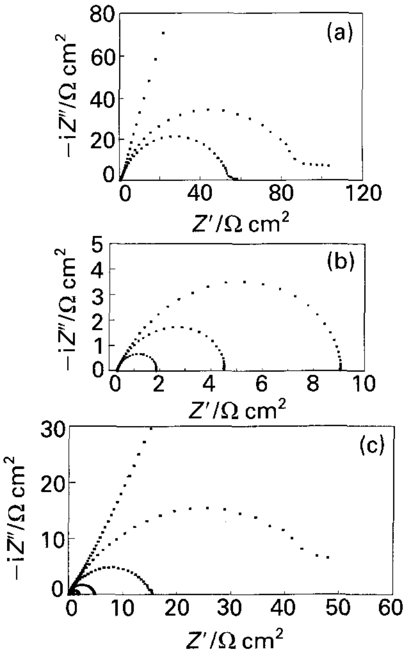

Fig. 5. Nyquist plots of Nafion® coated electrodes (0.5 mg Pt cm^{-2}) containing 20% and 30% PTFE loading, at various potentials: (a) 20% PTFE, 0.97, 0.91 and 0.87 V; (b) 20% PTFE, 0.81, 0.77 and 0.71 V; (c) 30% PTFE, 0.97, 0.91, 0.87, 0.81, 0.77 and 0.71 V.

Tafel slopes have been identified for the oxygen reduction process. At low current density, the process involves two electrons in the rate determining step (r.d.s.) whereas one electron is involved in the r.d.s. at large current densities. This reflects the change of the oxygen reduction kinetics from a Temkin condition, determined by the platinum coverage by oxide species at small overpotentials [4], to a Langmuir condition at large overpotentials. In the latter case the reduction process occurs on an oxide free platinum surface. The same behaviour has been observed for Nafion® filmed bare platinum electrode [4]. It is suggested that no impurities from the residual alcoholic solution remained entrapped in the porous catalyst structure after Nafion® impregnation and subsequent heat treatment. No correlation has been found between Tafel slopes and PTFE content; the values of charge transfer coefficient are close to 0.5 for both r.d.s.

The variation of the ohmic drop corrected overpotential as a function of the Teflon content, at various current densities upon correction for the diffusion limiting current, is shown in Fig. 4. The maximum activity is monitored for the electrode containing 30% PTFE as observed in Fig. 2, and a large increase of overpotential occurs upon increase of the PTFE content at 40%. The decrease of activity recorded for 40% PTFE, upon correction for ohmic drop and mass transfer, is lower than that shown in Fig. 2.

3.2. *a.c. Impedance spectroscopy*

To gain more details on this behaviour impedance spectra have been carried out on the Nafion® coated gas-diffusion electrodes, at various potentials, during the oxygen reduction process. The spectra are shown in Figs 5 and 6 in the Nyquist form. They mainly consist of one semicircle showing a constant phase element (CPE) at high frequencies [16]. The double layer capacitance (C_{dl}), the charge transfer resistance (R_{ct}) and the series resitance (R_s) of the electrodes measured at different potentials are reported in Table 2. The series resistance derives from the combination of the ionic resistance of the electrolyte and the electronic resistance of the electrode. As overpotential is increased, the charge transfer resistance and the relaxation times of the charge transfer process decrease, whereas the series resistance is almost constant at the various potentials (Table 2). The electrochemical parameters are dependent on the PTFE content of the electrodes. Linear relationships between the logarithm of R_{ct} and potential are observed at small overpotentials for the Nafion® coated electrodes. The slopes are 92.5,

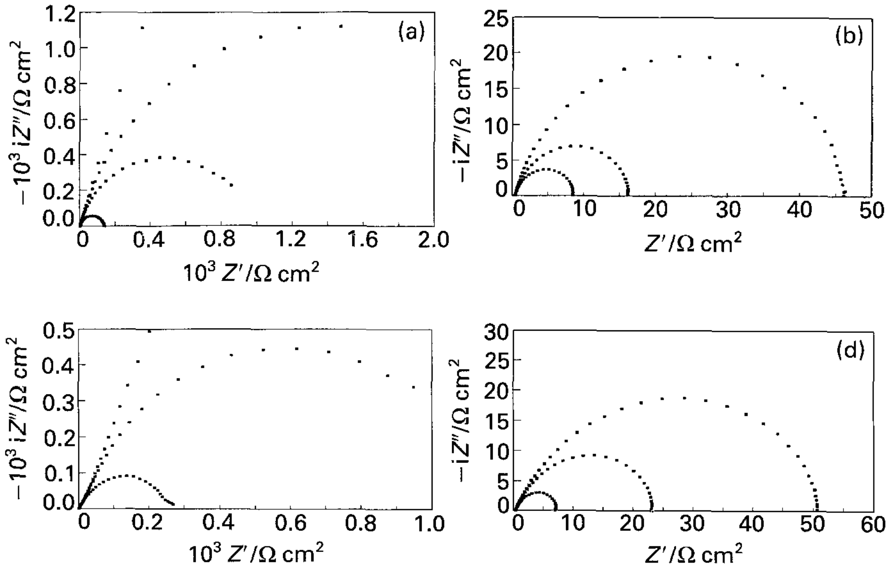

Fig. 6. Nyquist plots of Nafion® coated electrodes (0.5 mg Pt cm^{-2}) with 40% and 60% PTFE loading, at various potentials: (a) 40% PTFE, 0.97, 0.91, 0.87 and 0.81 V; (b) 40% PTFE, 0.77, 0.71 and 0.66 V; (c) 60% PTFE, 0.97, 0.91 and 0.87 V; (d) 60% PTFE, 0.81, 0.77 and 0.66 V.

Table 2. Impedance spectroscopy parameters for the oxygen reduction reaction on Pt/C electrocatalysts

*Electrode**	*Potential/V vs NHE*	$R_s/\Omega cm^2$	$R_{ct}/\Omega cm^2$	$C_{dl}/mF\,cm^{-2}$	f_{max}†/Hz
a	0.91	0.31	89.68	5.6	0.316
	0.87	0.33	53.18	4.75	0.631
	0.81	0.31	8.74	3.6	5.012
	0.77	0.31	4.21	3.0	12.589
	0.71	0.31	1.55	2.0	50.119
	0.66	0.31	1.35	–	–
b	0.91	0.3	48.9	16.28	0.2
	0.87	0.3	15.62	10.0	1.0
	0.81	0.3	4.68	4.28	7.943
	0.77	0.32	1.69	3.75	25.12
	0.71	0.32	0.84	3.0	63.0
	0.66	0.32	0.815	–	–
c	0.91	0.42	2797.0	4.5	0.0126
	0.87	0.41	963.0	3.3	0.0501
	0.81	0.4	138.6	2.29	0.5012
	0.77	0.4	45.6	2.2	1.585
	0.71	0.4	15.6	2.0	5.012
	0.66	0.4	8.18	1.95	10.0
d	0.91	0.42	1094	3.66	0.0398
	0.87	0.42	253	2.5	0.2512
	0.81	0.42	50	1.27	2.512
	0.77	0.42	22.7	0.88	7.943
	0.66	0.42	6.8	0.59	39.811
e	0.91	0.087	–	–	–
	0.87	0.083	624	6.41	0.0398
	0.81	0.083	59.07	6.77	0.3981
	0.77	0.084	23.0	6.92	1.0
	0.71	0.075	7.8	8.12	2.512
	0.66	0.07	3.8	10.52	3.981
f	0.91	0.275	170.62	14.8	0.0631
	0.87	0.281	71.25	14.1	0.1585
	0.81	0.278	21.22	6.28	1.0
	0.77	0.278	11.41	5.55	2.512
	0.71	0.275	6.288	6.36	3.981
	0.66	0.28	3.79	6.65	6.31
	0.61	0.27	2.662	5.98	10.0
g	0.91	0.29	214.77	18.6	0.0398
	0.87	0.29	99.47	16.0	0.1
	0.81	0.29	30.03	13.3	0.3981
	0.77	0.29	17.46	9.1	1.0
	0.66	0.29	5.96	6.7	3.981
	0.61	0.29	4.31	5.85	6.31

*As in Table 1.

†Relaxation frequency of the charge transfer process.

91, 81 and 78 mV (dec)$^{-1}$ for 30, 20, 60 and 40% PTFE containing electrodes, respectively. The impedance data suggest that oxygen reduction is kinetically favoured on 30% and 20% PTFE containing electrodes.

The lowest charge transfer resistance is recorded for the electrode with 30% PTFE in accordance with the d.c. polarization results. R_{ct} values for the electrode containing 60% PTFE are lower than those corresponding to the 40% PTFE electrode. This trend also appears in the d.c. polarization at low overpotentials (Fig. 1). The activity of 40% PTFE electrode surpasses that of the electrode with 60% PTFE at sustained currents, especially when the process becomes diffusion controlled. An increase of electrochemical activity for the oxygen reduction process in the kinetic region has been reported [13] for electrodes having high PTFE content. It has been attributed to surface-active substances contained in PTFE dispersion solution which can improve the distribution of platinum particles in the catalytic layer.

Impedance data show that the faradaic resistance is much larger than the series resistance at low overpotentials. The ionic resistance of the Nafion® electrolyte appears to be the main component of R_s (see below). It significantly limits the oxygen reduction process only at sustained currents; the ohmic loss can be evaluated in about 130 mV at 400 mA cm^{-2} for the electrode containing 30% PTFE. The series resistance increases slightly with the PTFE content, reaching 0.42 Ω cm^2 for the electrode containing 60% PTFE (Table 2).

The double layer capacitance was found to vary with the potential for Nafion® coated gas-diffusion

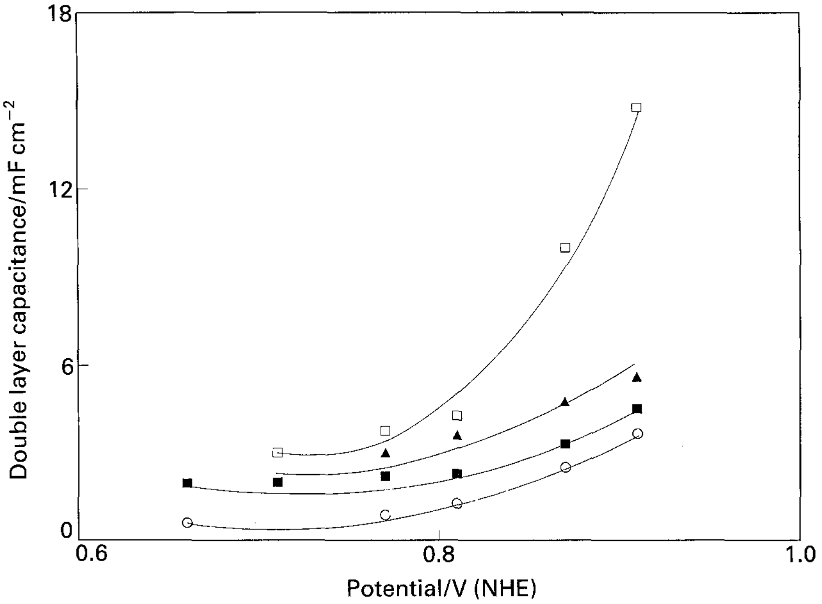

Fig. 7. Variation of the double layer capacitance as a function of the electrode potential, in the oxygen reduction process, on Nafion® coated gas-diffusion electrodes (0.5 mg Pt cm^{-2}) containing various PTFE amounts. Legend: (▲) 20%; (□) 30%; (■) 40%; (○) 60%.

electrodes; it decreases as the overpotential for the oxygen reduction is increased (Fig. 7). The electrode containing 30% PTFE showed the highest C_{dl} values. As observed, the active area determined by double layer capacitance does not necessarily correspond to the current generating surface [17]. Parthasarathy *et al.* [5] attributed the high capacitance values measured at low overpotentials on a Nafion® coated platinum microelectrode to a pseudocapacitive behaviour. In contrast, at high overpotentials the blocking effect by Nafion® of the active platinum sites determines low capacitance values [5].

3.3. *Nafion® coating and methanol crossover effects*

To better separate the different characteristics of Nafion® filmed and uncoated electrodes, a comparative study for samples containing low platinum loading (0.25 mg cm^{-2}) and optimum PTFE content (30%) was made. The effect of Nafion® film coating and methanol crossover through this film were investigated. The polarization curves in 2.5 M sulphuric acid, for the as-prepared and Nafion® coated electrodes, are shown in Fig. 8. The latter electrode has also been tested in 0.5 M CH_3OH solution.

The oxygen reduction process is more favoured, at low current densities, on the Nafion® coated electrode; the open circuit voltage is about 200 mV higher than the analogous uncoated electrode. At current densities higher than 100 mA cm^{-2}, the activity of the as-prepared electrode surpasses that of the Nafion® coated electrode (Fig. 8). The positive effect generated by the Nafion® film coating at low current densities is observed, even in presence of methanol (0.5 M) in solution; in fact, no significant loss of activity is recorded with respect to the uncoated electrode. The increase of overpotential for the Nafion®-coated electrode becomes quite considerable at high current densities. The mass transfer and ohmic drop corrected curves (Fig. 9) show that the

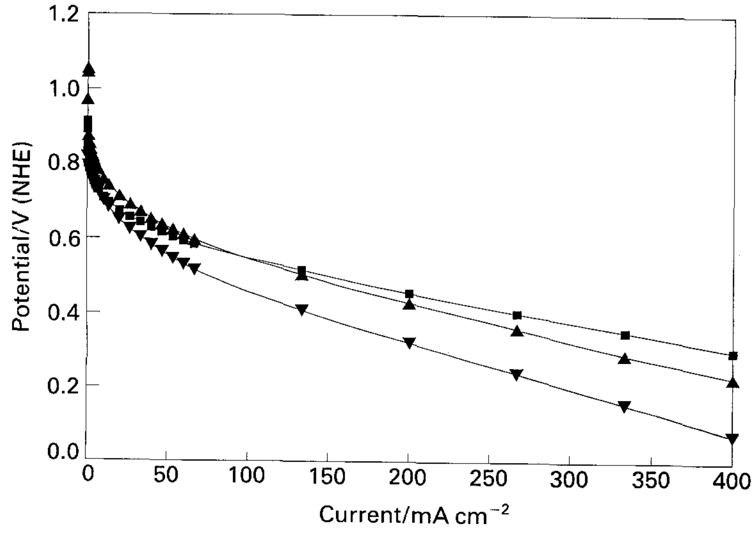

Fig. 8. Galvanostatic steady-state polarization curves, for the oxygen reduction at 60 °C, on Pt/C electrodes (0.25 mg Pt cm^{-2}). Legend: (■) Uncoated; (▲) Nafion® coated; (▼) Nafion®-filmed electrode immersed in methanol.

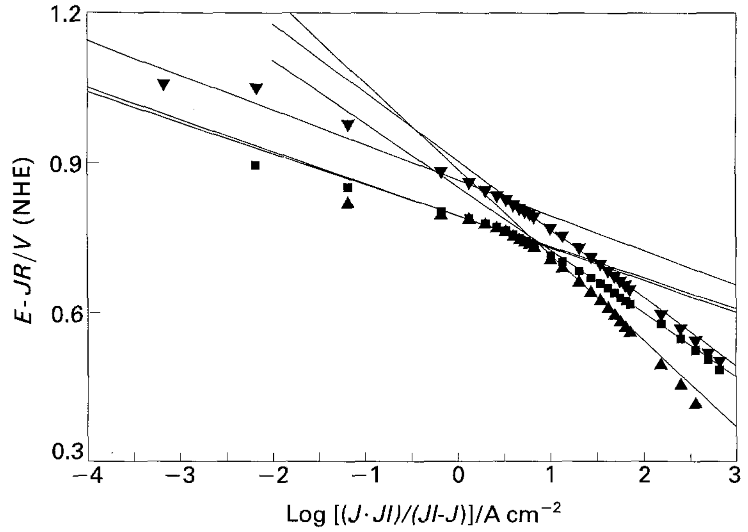

Fig. 9. Tafel plots for oxygen reduction at 60 °C on Pt/C electrodes (0.25 mg Pt cm^{-2}). Legend: (▼) Nafion®-coated electrode; (■) uncoated electrode; and (▲) Nafion® filmed electrode immersed in methanol.

kinetic activity of the Nafion®-coated electrode is higher than that of the as-prepared electrode up to 300 mA cm^{-2}. These results indicate that ohmic drop and mass transfer control reduce significantly the activity of Nafion®-coated electrodes at high currents.

The ohmic drop in the Nafion® filmed electrodes is mainly due to the ionic resistance. This can be observed by comparing the values of the electrode series resistance obtained from the impedance spectra of the as-prepared and filmed electrodes (Table 2). The impedance spectra of Nafion®-coated electrodes show a more accentuated constant phase element at high frequencies, with respect to the uncoated electrodes (Fig. 10). The impedance spectra of Nafion®-coated electrodes show a shape like that calculated by Springer *et al.* using a dynamic model of the cathode operation in a SPE® fuel cell [18]. These authors determined a theoretical 45° phase shift at high frequency in the Nyquist plots and attributed it to the effects of the distributed ionic resistance and double layer capacitance. Fig. 11(a, b) shows a non-linear least square fitting of the measured frequency dispersion for a Nafion® coated electrode. The equivalent circuit is composed of a series resistance (R_s), double layer capacitance (C_{dl}) in parallel with a series combination of the charge transfer resistance (R_{ct}) and a constant phase element (CPE). The element associated with the double layer capacitance is not actually a pure capacitor, having a power dependence on frequency of its transfer function slightly lower than 1 (admittance mode). The constant phase element is generally observed in the impedance spectra of materials with large porosity and is related to the distributed character of the electrochemical process [19, 20]. In the present study, the observation of a more accentuated constant phase element in the spectra of Nafion® filmed electrodes with respect to uncoated electrodes could be related to the finite-diffusion effects caused by the Nafion® membrane [5].

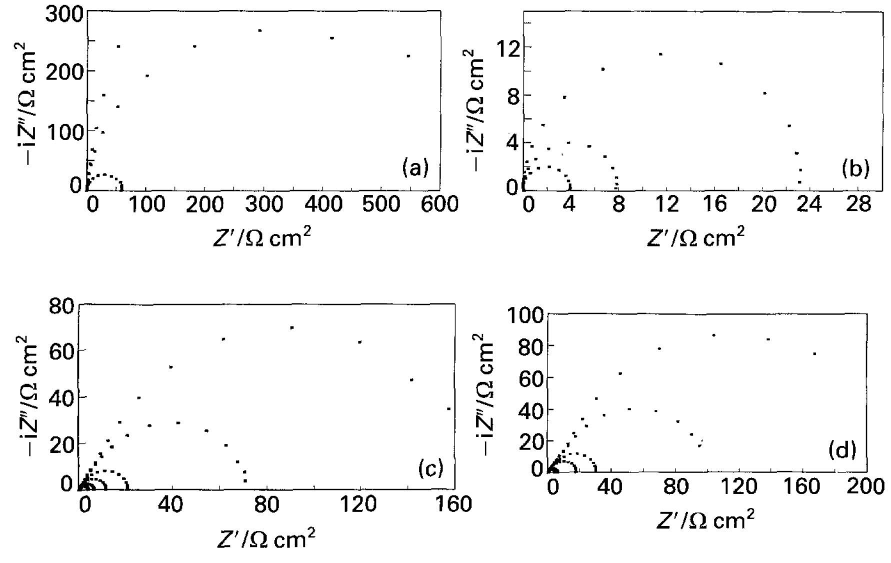

Fig. 10. Nyquist plots of uncoated and Nafion coated electrodes, at 60 °C on Pt/C electrodes (0.25 mg Pt cm^{-2}) with 30% PTFE loading, at various potentials. (a) Uncoated: 0.91, 0.87 and 0.81 V; (b) uncoated: 0.77, 0.71 and 0.66 V; (c) Nafion® coated: 0.91, 0.87, 0.81, 0.77, 0.71 and 0.66 V; (d) Nafion® coated electrode immersed in methanol: 0.91, 0.87, 0.81, 0.77, 0.66 and 0.61 V.

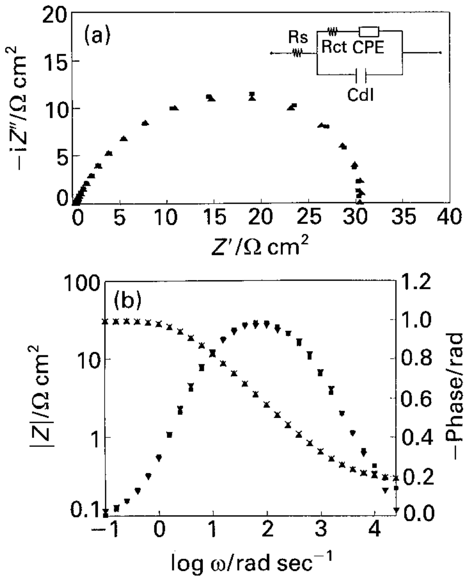

Fig. 11. (a) Nyquist plot of the measured (■) and simulated (▲) frequency dispersion for a Nafion® coated gas-diffusion electrode immersed in methanol, during the oxygen reduction process (0.81 V vs NHE). The inset shows the equivalent circuit. (b) Bode plot of the measured (▲, ▼) and simulated (×, ■) modulus and phase-shift, respectively, of the impedance response.

The behaviour observed in the polarization curves (Fig. 8) for the coated and uncoated electrodes is in agreement with that found with a Nafion®-filmed rotating disc electrode in sulphuric acid [1]. These phenomena have been interpreted on the basis of the large oxygen solubility at the Nafion® electrolyte–electrode interface that causes a decrease of overpotential at low current density [1]. At the same time the Nafion® film reduces the number of active sites in contact with the electrolyte and hinders the diffusion of reactive species. Hence, an increase in overpotential is recorded at high currents where these latter effects become predominant. The Tafel slope obtained at low overpotentials in the presence of methanol differs only slightly from that for the previous Nafion®-coated electrode, even if the corresponding polarization curve is cathodically shifted, probably due to a poisoning effect originated by methanol crossover through the film (Fig. 9). At high current densities, in the presence of methanol, the Tafel slope (−172.28 mV) shifts considerably from the theoretical one electron process (−132 mV at 60 °C). The observed behaviour may be interpreted as a function of the variation of the Pt–O bond strength with potential. It is known that, at high potentials, oxygen is strongly chemisorbed on platinum [21]; this is not a favourable condition for CH_3OH oxidation. As observed in cyclic voltammetry experiments [21], at potentials lower than those corresponding to Pt-oxide reduction, methanol is oxidized even in cathodic polarization. In this potential region, the formation of labile oxygen on the platinum surface is favoured. It can be deduced, from Fig. 9, that, when oxygen reduction occurs in a Temkin condition, i.e. platinum is covered by chemisorbed oxygen species (two electrons are involved in the r.d.s.), methanol produces only a blocking effect for some platinum sites at the surface. In the region where the platinum surface is free from strongly adsorbed oxygen species and the oxygen reduction process occurs under Langmuir conditions, methanol is probably oxidized at the cathode. Nafion® provides a suitable potential region where platinum is covered by strongly bonded oxygen. Here phenomena related to cathode deactivation in methanol fuel cells are significantly reduced.

This picture is confirmed by the analysis of the charge transfer resistance derived from the impedance spectra at various potentials for these electrodes. At low overpotentials, R_{ct} values are smaller for the Nafion®-coated electrodes with respect to the

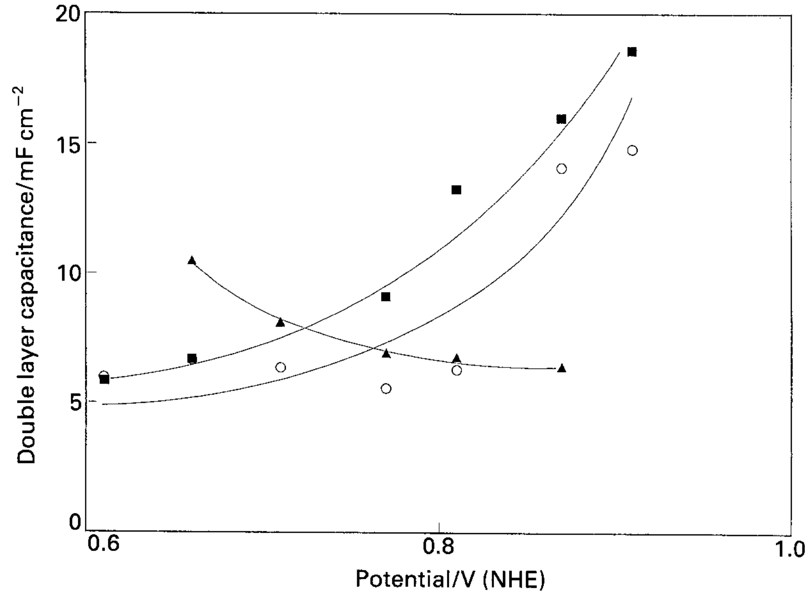

Fig. 12. Variation of the double layer capacitance with the potential for the oxygen reduction on Nafion® coated (○), Nafion coated immersed in methanol (■) and uncoated (▲) gas-diffusion electrodes (0.25 mg Pt cm^{-2}).

uncoated electrode, even in the presence of methanol in solution (Table 2). In the kinetic region, the logarithm of the charge transfer resistance varies almost linearly with potential and shows a similar slope for both the Nafion®-coated (also upon immersion in methanol) and uncoated electrodes. This suggests that methanol does not produce a change in the reaction mechanism in this region, in accordance with the d.c. polarization data. At high overpotentials, the charge transfer resistance for Nafion®-filmed electrodes deviates significantly from the linear behaviour, probably due to the onset of diffusion control. This occurs to a lower extent for the uncoated electrode.

A significant difference is found in the behaviour of the double layer capacitance in Nafion® filmed electrodes and uncoated electrodes; filmed electrodes show higher capacitance values and a decrease of C_{dl} with increase of overpotential (Fig. 12). An opposite behaviour is observed for the uncoated electrode. The highest C_{dl} values are recorded for the Nafion® electrode immersed in methanol. Probably the presence of methanol increases the pseudo-capacitance at positive potentials.

References

[1] S. Gottesfeld, I. D. Raistrick and S. Srinivasan, *J. Electrochem. Soc.* **134** (1987) 1455.

[2] D. R. Lawson, L. D. Whiteley, C. R. Martin, M. N. Szentirmay and J. I. Song, *ibid.* **135** (1988) 2247.

[3] W. Paik, T. E. Springer and S. Srinivasan, *ibid.* **136** (1989) 644.

[4] A. Parthasarathy, C. R. Martin and S. Srinivasan, *ibid.* **138** (1991) 916.

[5] A. Parthasarathy, B. Davé, S. Srinivasan, A. J. Appleby and C. R. Martin, *ibid.* **139** (1992) 1634.

[6] E. A. Ticianelli, J. G. Beery, S. Srinivasan, *J. Appl. Electrochem.* **21** (1991) 597.

[7] S. Srinivasan, E. A. Ticianelli, C. R. Derouin and A. Redondo, *J. Power Sources* **22** (1988) 359.

[8] J. B. Goodenough, A. Hamnett, B. J. Kennedy, R. Manoharan and S. A. Weeks, *J. Electroanal. Chem.* **240** (1988) 133.

[9] A. Parthasarathy, S. Srinivasan, A. J. Appleby and C. R. Martin, *J. Electrochem. Soc.* **139** (1992) 2530.

[10] P. Zelenay, B. R. Scharifker, J. O'M. Bockris and D. Gervasio, *ibid.* **133** (1986) 2262.

[11] Z. Poltarzewski, P. Staiti, V. Alderucci, W. Wieczorek and N. Giordano, *ibid.* **139** (1992) 3.

[12] Y. Gao, F. Noguchi, T. Mitamura and H. Kita, *Electrochim. Acta* **37** (1992) 1327.

[13] T. Maoka, *ibid.* **33** (1988) 379.

[14] S. Motoo, I. Fujihara and N. Furuya, Proceedings of the 50th Annual Meeting of the Electrochemical Society, Japan, *Abstracts A113* (1983).

[15] W. M. Vogel and K. A. Klinedinst, *Electrochim. Acta* **22** (1977) 1385.

[16] I. D. Raistrick, *J. Electrochem. Soc.* **35** (1990) 1579.

[17] R. Holze and W. Vielstich, *Electrochim. Acta* **29** (1984) 607.

[18] T. E. Springer, S. Gottesfeld and T. Zawodzinski, Proceedings of the 182nd Meeting of The Electrochemical Society, Toronto, October (1992), *Extended Abstract No. 92*, p. 144.

[19] T. E. Springer and I. D. Raistrick, Proceedings of the Second Symposium on Electrode Materials and Processes for Energy Conversion, (edited by S. Srinivasan, S. Wagner and H. Wroblowa), The Electrochemcial Society Softbound Proceedings Series, Pennington, NJ (1987) PV 87–12, p. 152.

[20] A. S. Aricò, V. Alderucci, V. Antonucci, S. Ferrara, V. Recupero, N. Giordanò and K. Kinoshita, *Electrochim. Acta* **37** (1992) 523.

[21] D. Pletcher and V. Solis, *Electrochim. Acta* **27** (1982) 775.