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A Nafion®-bound platinized carbon electrode for oxygen reduction in solid polymer electrolyte cells

A. K. SHUKLA[1], P. STEVENS, A. HAMNETT, J. B. GOODENOUGH[2]

Inorganic Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QR, UK

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A full-factorial statistical method has been used to optimize the amount of binder, the compaction load and the compaction time in order to fabricate Nafion®-bound carbon electrodes containing platinum and pyrolysed cobalt *meso*-tetramethoxyphenylporphyrin (CoTMPP). These electrodes are designed for oxygen reduction in solid polymer electrolyte fuel cells, and it has been found that incorporation of Nafion® gel with the carbon substrate facilitates its binding with the Nafion® membrane of such a fuel cell. The polarization behaviour of a Nafion®-bound carbon electrode containing platinum is compared to that containing pyrolysed CoTMPP.

1. Introduction

Solid polymer electrolyte fuel cells (SPEFCs) hold certain advantages over those with immobilized electrolytes as they provide: (a) a non-volatile electrolyte below 100° C; (b) a drastic reduction in corrosion and materials-related problems; (c) negligible electrolyte leaching (as water is the only reaction product); (d) a thin electrolyte layer. Polymer electrolytes have excellent oxygen solubility and diffusivity characteristics, and they are therefore expected to yield better performance than conventional acid fuel cells, provided the oxygen can be hindered from reaching the hydrogen electrode [1, 2].

One of the problems associated with the development of commercial SPEFCs is the more efficient use of platinum electrocatalyst. The use of pure platinum black is wasteful, and it is necessary to use a supported catalyst instead. Active carbons have frequently been employed as supports and their use in conventional acid fuel cells is now well established [3]. The most common SPE employed in fuel cells is Nafion®, a polyperfluorosulphonic acid hydrated polymer [4]. However, Nafion® membranes do not wet the carbon supports well, which causes difficulty in binding the polymer onto these supports.

This communication describes an attempt to develop an optimized porous carbon electrode that is dispersed with platinum catalyst and is bound to the Nafion® membrane. In an earlier optimization study on a porous carbon fuel cell electrode, it was found that the factors that mainly govern the porous structure are the amount of PTFE binder and the load and time of compaction [5]. In this study, therefore, we have conducted a full-factorial design [5] experiment to optimize the structure of the electrode with respect to these three variables. The other parameters – namely the size of the carbon particles, the mixing time of the binder and the pressure of the oxygen feed gas – have been kept constant at pre-decided levels during the experiment. The unique feature of these electrode preparations is the incorporation of Nafion® gel with the platinized carbon and the PTFE binder. The gel helps to bind the Nafion® membrane to the platinum-catalysed carbon, and enables the porous carbon to be integrated to the electrolyte. The necessary interface between the catalyst, the carbon, the hydrophobic binder and the solid electrolyte is achieved by this method.

The electrodes have been tested for electroreduction of oxygen in the range 40–90° C and are found to be capable of sustaining load current densities of about $250\,\mathrm{mA\,cm^{-2}}$ at 60° C with a polarization of less than 300 mV from the rest potential of 0.98 V vs the dynamic hydrogen electrode (DHE). The performance of the electrode with pyrolysed CoTMPP catalyst impregnated on the carbon has also been examined.

2. Experimental details

2.1. *Preparation and electrochemical characterization of platinized carbon electrodes in 2.5 M H_2SO_4*

The platinized carbon electrodes were prepared from Vulcan XC-72 carbon comminuted by heat treating at 930° C in flowing CO_2. This treatment resulted in a weight loss of 27%. In order to reduce the number of variables in the optimization of the Nafion®-bound electrodes, the electrodes were initially fabricated without Nafion® and tested in 2.5 M H_2SO_4. From these data, the compaction time, the compaction load and the amount of PTFE binder were simultaneously

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[1] On leave from Solid-State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, India.

[2] Present address: Department of Materials Science and Engineering, ETC 5.160, The University of Texas at Austin, Austin, Texas 78712-1084, USA.

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Table 1. Test conditions for the 2^3-factorial design and the corresponding polarization data

Test conditions			Design matrix[1]	Code	Current densities ($mA\,cm^{-2}$) and corresponding polarization potential (mV vs DHE)					
A (kg)	B (min)	C (wt %)			88.5	177	265.5	354	442.5	531
300	1	25	− − −	(1)	709	634	566	460	336	242
500	1	25	+ − −	a	712	651	604	568	537	481
300	5	25	− + −	b	741	680	630	572	518	458
500	5	25	+ + −	ab	748	694	651	550	413	-
300	1	40	− − +	c	590	470	361	252	165	-
500	1	40	+ − +	ac	664	568	502	423	363	298
300	5	40	− + +	bc	727	686	643	569	530	368
500	5	40	+ + +	abc	752	660	600	541	490	452

[1] − refers to lower limit and + to upper limit of of variation range.

optimized as desribed below. Using these parameters, Nafion®-bound electrodes were fabricated with varying amounts of Nafion, and further optimization of the electrode with respect to the proportion of Nafion® was effected.

The electrodes used for testing in 2.5 M H_2SO_4 were made by depositing 7 wt % platinum metal onto the pretreated carbon; this was achieved by reducing a solution of hexachloroplatinic acid with sodium formate in the presence of a suspension of the carbon [6]. A suspension of PTFE binder (ICI Fluon-GP2) was then added and the electrodes fabricated as described elsewhere [7], the final step being compaction onto a platinum mesh (390 aperture cm^{-2}, wire diameter 0.13 mm) according to the design matrix of Table 1.

The configuration of the electrochemical cell used for the present study is very similar to that described elswhere [8]: platinum mesh was employed as the counter electrode and a dynamic hydrogen electrode (DHE) was used as the reference electrode. Steady-state current potential curves for the various electrodes were obtained galvanostatically at 40° C with oxygen being admitted from the rear of the electrode at a pressure of 10 mm Hg. These curves were not corrected for *iR* drop.

2.2. *The statistical method*

The porous electrodes employed in the present study were all fabricated under the specific conditions given in Table 1. These conditions influence the polarization behaviour of the electrodes (measured as the deviation of the electrode potential from the rest potential at a given current), and this deviation can be expressed as

$$y = f(x_1, x_2, \ldots, x_n) \qquad (1)$$

where the x_i's are the input parameters. In order to simplify the analysis, it is common to define normalized parameters x_i^* for a two-level system as:

$$x_i^* = \frac{x_i - [x_i(+) + x_i(-)]/2}{[x_i(+) - x_i(-)]/2} \qquad (2)$$

where $x_i(+)$ and $x_i(-)$ are the upper and lower limits of the x_i's and optimization is most effectively performed within these limits. It is evident that x_i^* will take the value $+1$ when $x_i = x_i(+)$ and -1 when $x_i = x_i(-)$. If a polynomial relationship exists between y and the x_is or, equivalently, the x_i^*'s, Equation 1 may be written in the form:

$$y = m_0 + \sum_i m_i x_i^* + \sum_j \sum_{i<j} m_{ij} x_i^* x_j^* + \ldots + m_{123\ldots n} x_1^* x_2^* \ldots x_n^* \qquad (3)$$

where the factors $m_1, \ldots m_n$ in Equation 3 describe the effect of the individual parameters and the $m_{ij}, \ldots, m_{ijk}, \ldots$ etc. describe the effect of the coupled action of the parameters. In this scheme, an optimum is found for the various input parameters under the assumption that the respective changes are linear.

Table 2. Yates' analysis of the polarization data in Table 1 at 265.5 $mA\,cm^{-2}$

Treatment code	Results (V vs DHS)	Yates' analysis of the data			Mean difference (III/4)	Total effect
		I	II	III		
(1)	0.566	1.170	2.451	4.557	1.139	-
a	0.604	1.281	2.106	0.157	0.039	A
b	0.630	0.863	0.059	0.491	0.123	B
ab	0.651	1.243	0.098	−0.201	−0.050	AB
c	0.361	0.038	0.111	−0.345	−0.086	C
ac	0.502	0.021	0.380	0.039	0.010	AC
bc	0.643	0.141	−0.017	0.269	0.067	BC
abc	0.600	−0.043	−0.184	−0.167	−0.042	ABC
Total	4.557				0.061	

Table 3. Test condition for the final optimization

Trial No.	*A* *(min)*	*B* *(kg)*	*C* *(wt %)*
1	3	400	32.5
2	4	415	30.0
3	5	430	27.0
4	6	445	24.0

In the present study, the parameters to be optimized were: (A) compaction load; (B) compaction time; (C) amount of binder. The other variables such as the size of the carbon particles, the compaction temperature and the pressure of oxygen were kept constant. The levels fixed for the parameters A, B and C are given in Table 1 and the full 2^3-factorial design required eight trial runs: one average effect, three main effects, three first-order effects and one second-order effect [9].

2.3. *Preparation and electrochemical characterization of Nafion®-bound platinized carbon electrodes*

The statistical analysis carried out in 2.5 M H_2SO_4 led, as described below, to an optimum compaction pressure of 400 kg, an optimum compaction time of 5 min, and an optimum PTFE-binder loading of 27 wt %. It was found that electrodes fabricated using these conditions gave excellent results in 2.5 M H_2SO_4 over the whole temperature range explored (40–90° C) and further optimization for each operating temperature was judged, therefore, not to be necessary.

The Nafion®-bound electrodes were fabricated from an admixture of pre-treated carbon, platinized to 7 wt % as described above, and bound with Nafion® gel and 27 wt % PTFE. The Nafion® gel was prepared from a solution of Nafion® 117 in ethanol/water by evaporating to remove the ethanol and concentrating the resultant solution to 16 wt % Nafion®. Varying proportions of this, to produce electrodes containing 5–20 wt % (dry weight) Nafion® gel, were mixed with the platinized carbon and PTFE and the electrodes (of area 2.4 cm^2) were hot-pressed for 5 min at 95° C and 400 kg between platinum mesh (as specified above) on one side and Nafion® 117 membrane (which had been pre-treated by boiling in dilute H_2SO_4 for an hour to convert it to the protonic form) on the other side. Hot pressing the entire package dehydrates the Nafion® gel to a form more like the membrane, and effectively 'welds' the gel onto the membrane.

The electrochemical performance of these half-cell electrodes for oxygen reduction was tested by immersing the package in 2.5 M H_2SO_4. The Nafion® membrane prevented direct contact between the acid electrolyte and the porous carbon electrode, but a somewhat higher oxygen pressure (20 mm Hg) was found necessary to obtain reasonable current densities. Polarization curves were obtained at temperatures between 60 and 90° C, and the optimum proportion of dehydrated Nafion® gel was found to be 14 wt %.

3. Results and discussion

A summary of the electrochemical polarization data for oxygen reduction in 2.5 M H_2SO_4 on various test electrodes fabricated without Nafion® is presented in Table 1, and the Yates' analysis of these data is presented in Table 2. From the analysis of the data in Table 2, it can be seen that: (i) by increasing the compaction load from 300 to 500 kg, the electrode performance could be increased by an average amount of only 39 mV; (ii) by increasing the compaction time from 1 to 5 min, the electrode performance could be increased by an average amount of 123 mV; and (iii) by reducing the amount of binder (in the present case PTFE) from 40 to 25 wt %, the electrode performance could be increased by 86 mV. At this stage, both simple and discriminating statistical tests were conducted to determine the significance of the main effects

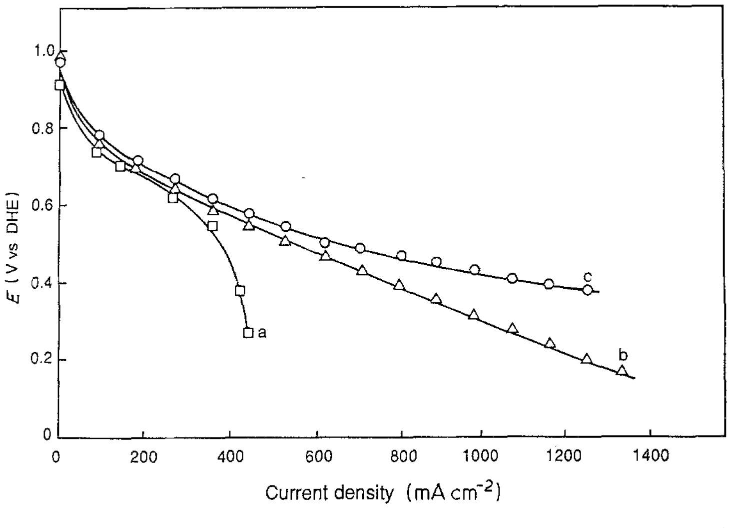

Fig. 1. Oxygen reduction polarization curve for supported platinum electrode at 40° C, 85 mm water (10 mm Hg) of oxygen above atmospheric pressure fabricated under the following conditions: (a) 415 kg compaction load, 4 min compaction time, 30% wt PTFE; (b) 400 kg compaction load, 3 min compaction time, 32.5 wt % PTFE; (c) 400 kg compaction load, 5 min compaction time, 27 wt % PTFE.

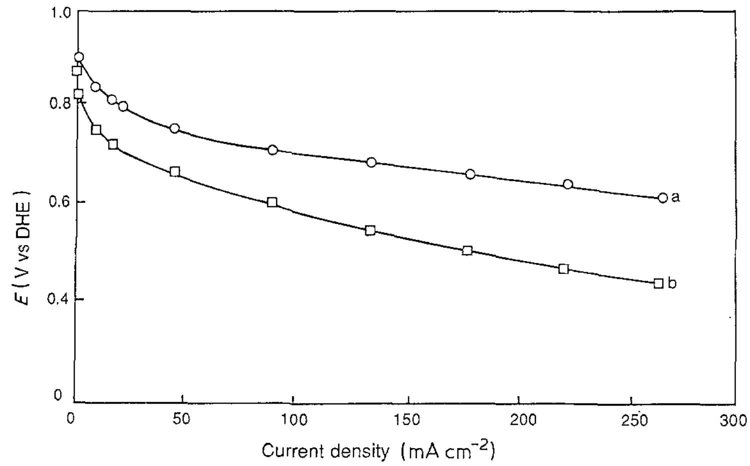

Fig. 2. Oxygen reduction polarization curves (no *iR* compensation) for Nafion®-bonded electrodes, 20 mm Hg of oxygen, 60° C, fabricated under optimum condtions: (a) with platinum catalyst; (b) with pyrolysed CoTMPP.

considered in the design scheme. The $2N^{1/2}$ test [9] suggested that compaction time was the dominant effect. If we increase the compaction time in 1 min intervals from its mean value of 3 min then the compaction load should be increased in steps of 15.6 kg and the binder composition decreased by 2.7 wt % *pro rata* from their respective mean values. Accordingly, experiments with the test conditions indicated in Table 3 were conducted, and an optimum found between the trial conditions 1 and 2.

The compaction pressure was then fixed at 400 kg and the compaction time and binder composition were varied *pro rata*, and these final experiments suggested that the optimum values for the parameters A, B and C were 400 kg, 5 min and 27 wt % respectively. The polarization curves for the electrodes investigated in the final stages of the optimization are shown in Fig. 1. A check on the fit of the data given in Table 2 suggests that the analysis is correct.

The polarization curves for oxygen reduction with the Nafion®-bound platinized carbon electrode fabricated with the optimum conditions of the previous paragraph and with 14 wt % dehydrated Nafion® gel is shown in Fig. 2. There was little effect on the performance of these electrodes as the cell temperature was increased from 60 to 90° C. The electrodes, on constant current of 100 mA cm^{-2} for 120 h with current interruptions every 24 h (to open circuit), polarized 50 mV from the initial value. Higher load currents could be sustained.

Preliminary polarization studies with PTFE-bound Nafion®-incorporated carbon electrodes catalysed with CoTMPP were encouraging. The polarization curve is also shown in Fig. 2 along with the corresponding curves for platinized carbon electrode. This electrode polarized by 50 mV after 120 h at a current density of 100 mA cm^{-2} and current interruption (to open circuit) for 10 s every 30 min.

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