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Fractional-factorial design of a porous-carbon fuel-cell electrode

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The use of fractional-factorial methods in the optimization of porous-carbon electrode structure is discussed with respect to weight-loss of carbon during gas treatment, weight and mixing time of binder, compaction temperature, time and pressure, and pressure of feed gas. The experimental optimization of an air electrode in alkaline solution is described.

1. Introduction

Porous electrodes form an important component of many electrochemical systems which include batteries, fuel cells, electrolytic cells, and electrowinning, electro-organic synthesis and gas-evolving systems. Porous-electrode strength, weight, cost, durability and a host of performance characteristics are significantly influenced by the extent and nature of porosity which needs to be optimized for a specific end use. Such an optimization becomes difficult, especially when a combination of two or more parameters at two to three levels is desired. For example, porous-carbon electrodes for fuel cells need an optimization of parameters such as the degree of mixing of carbon and binder, the degree of compaction of electrodes and the gas permeability.

It has been noticed that even minor variations in the preparation of porous electrodes induce large variations in their performance. Determining the optimum values of the parameters for preparation of such electrodes is critical. In this context statistical methods have been found useful [1–3], and among these methods factorial and simplex algorithms are the most commonly used.

If the response function varies linearly with the parameters, then the number of degrees of freedom for error in a 2^k full-factorial design is $2^k - k - 1$ where k is the number of parameters and 2 the number of levels taken in the design [4]. The other uses of the degrees of freedom are in estimating interaction coefficients and in testing for a lack-of-fit. In each case, error estimates can be obtained either by adding experiments at the centre of the design or by replication of the data points. It is this flexibility that makes it so useful a method.

By contrast, the simplex design has a redundancy (the ratio of available degrees of freedom to the degrees of freedom associated with the model) of exactly unity and there are no degrees of freedom to make either an error estimate or to estimate the fit of the model. In fact, the model fits the data exactly and there are no residuals. Thus, although the simplex design provides an easy estimate of major effects, it does not guarantee that the estimate adequately represents the data. Clearly, the major disadvantage of the factorial method is that the number of trial runs required in a 2^k full-factorial design increases geometrically with k. However, when k is not small the desired information can often be obtained by performing a fraction of the full-factorial design. This paper describes an attempt to fabricate a porous-carbon fuel-cell electrode employing a 2^{7-3} fractional-factorial design.

2. Experimental details

2.1. *Preparation and electrochemical characterization of porous-carbon electrodes*

Activated coconut-shell charcoal was prepared as described previously [5]. In brief, it was subjected to gravity separation with saturated calcium chloride solution and then repeatedly extracted with azeotropic HCl followed by distilled water. It was subsequently comminuted by treating with CO_2 gas at 900° C for specified periods. The desired compositions of the catalyst were deposited on to the carbon substrate by reducing their respective salt solutions with sodium formate [6–8]. Electrodes were compacted with various specimens of the carbon by hot pressing with polyethylene binder on expanded metal-screens [7]. The details of the electrochemical cell employed during the present study are described in an earlier publication [9]. The electrolyte used is aqueous KOH (1 M for optimization runs) which was stirred mechanically. Sintered nickel electrodes were employed as counter electrodes and a $Hg/HgO,OH^-$ electrode as

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the reference electrode. Steady-state current potential curves for various test electrodes were obtained galvanostatically for the desired analysis and design; they were not *iR* corrected.

2.2. *The statistical method*

Porous-carbon electrodes employed in the present study were fabricated under specific physical and chemical conditions. These conditions influence the polarization behaviour of the electrode (deviation from the rest potential at a given current in the galvanostatic experiment), which could be expressed as,

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

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

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

where $x_i(+)$ and $x_i(-)$ are the upper and lower limits of x_i and optimization will be most effectively performed within these limits. It is evident that x_i^* will take the value $+1$ when $x_i = x_i(+)$ and -1 where $x_i = x_i(-)$.

We now suppose that a polynomial relationship exists between y and the x_i, or equivalently, the x_i^* [2, 3, 10] of the form

$$y = m_0 + \sum_i m_i x_i^* + \sum_{i<j}\sum m_{ij} x_i^* x_j^* + \ldots + m_{123\ldots n} x_1^* x_2^* \ldots x_n^* \qquad (2)$$

where the m-factors in equation (2) describe the effect of the individual parameters ($m_1, \ldots, m_n$) and the effect of the coupled action of parameters ($m_{ij}, m_{ijk} \ldots$), these coupled actions will be referred to as higher-order interactions. To reduce the number of experiments, higher-order interactions can be confounded with the individual parameters [11–13]. In this scheme an optimum is found for the various input parameters within the range covered by each of these parameters and under the assumptions of equation (2).

In this study it was decided to study seven parameters namely (A) %-weight loss of carbon during gas comminution – a parameter related to the particle size of carbon; (B) %-weight of polyethylene binder (mean particle-size 20 μm); (C) mixing time of carbon with binder; (D) compaction temperature of the electrodes; (E) compaction pressure for the electrodes; (F) compaction time for the electrodes, and (G) pressure of feed gas. Levels fixed for these parameters are given in Table 1. The full 2^7-factorial design would have required 128 trial runs comprising of: one average effect; 7 mean effects; 21 first-order, 35 second-order, 35 third-order, 21 fourth-order, 7 fifth-order and 1 sixth-order interaction effects. Experimentally this is prohibitive. However, it is possible to reduce the trial runs quite substantially by confounding the higher-order interactions with the individual parameters. In the present case, it is found that each individual parameter is always confounded with four third-order interactions and each second-order interaction is confounded with two further second-order interactions. The remaining third-order interactions are confounded to each other. Interactions from fourth-order and higher are not included as they are confounded with one or the other of the above interaction effects. Thus only 16 trial runs need be carried out. Such a design is called a 2^{7-3} fractional factorial design [11–13]. The test matrix for the 2^{7-3} fractional-factorial design along with the confounding scheme is given in Table 2.

3. Results and discussion

The results of various trials together with the Yates' analysis of the data for oxygen reduction on bare (without any catalyst) carbon electrode in 1 M KOH at 30° C are given in Table 3. The first step is to arrange the average potentials of the electrodes at a fixed load current-density in the standard order as in column 2 of Table 3, and then derive in turn columns 3, 4, 5 and 6; the first half of column 3 is derived from the response column 2 by summing successive pairs in column 2 and the second half by differencing successive pairs in column 2, and other columns are each derived from the previous one in the same way. A check on the analysis is possible by comparing the corrected sums of squares for the 16 results and the total of the sum of the squares given in column 9. It is seen from Table 3 that the two values match within round-off errors.

The mean-effect values given in column 7 of Table 3 indicate the relative effects of each of the parameters

Table 1. Values of individual parameters at two levels

Levels	*% wt loss of carbon on gas treatment* (A) (wt %)	*% wt of polyethylene binder* (B) (wt %)	*Mixing time of the carbon and binder* (C) (sec)	*Compaction temperature for the electrode* (D) (K)	*Compaction pressure for the electrode* (E) (kg m^{-2})	*Compaction time (the time for which load was retained)* (F) (sec)	*Pressure of the feed gas* (G) (N m^{-2})
Low (–)	46	18	1800	373	400 000	0	1333
High (+)	75	30	3600	423	600 000	600	7997

Table 2. Test matrix for the 2^{7-3} fractional-factorial design of porous-carbon electrode

Individual parameters	*Electrodes with sixteen different treatment combinations*																
	Electrode No. (trials)	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8	E_9	E_{10}	E_{11}	E_{12}	E_{13}	E_{14}	E_{15}	E_{16}
	Treatment combination	0^a	1^b	2^b	12^c	3^b	13^c	23^c	4^b	5^b	15^c	6^b	16^c	7^b	17^c	27^c	127^d
A		+	+	−	−	+	+	−	−	+	+	−	−	+	+	−	−
B		+	+	+	+	−	−	−	−	+	+	+	+	−	−	−	−
C		+	+	+	+	+	+	+	+	−	−	−	−	−	−	−	−
D		+	+	−	−	−	−	+	+	−	−	+	+	+	+	−	−
E		+	−	+	−	−	+	−	+	−	+	+	−	−	+	−	+
F		+	−	−	+	+	−	−	+	−	+	−	+	+	−	−	+
G		+	−	−	+	−	+	+	−	+	−	+	−	+	−	−	+
Confounding scheme																	
2-factor interactions					34^c 56^c		24^c 57^c	14^c 67^c			26^c 37^c		25^c 47^c		35^c 46^c	36^c 45^c	
3-factor interactions			234^d 256^d 357^d 467^d	134^d 156^d 367^d 457^d		124^d 157^d 267^d 456^d			123^d 167^d 257^d 356^d	126^d 247^d 346^d 137^d		125^d 147^d 237^d 345^d		135^d 146^d 236^d 245^d			136^d 347^d 567^d 246^d 235^d 145^d

[a] Average effect; [b] Main effects comprising of individual parameters; [c] 2-factor interactions; [d] 3-factor interactions.

and their interactions. To obtain the optimum, a parameter must be shifted to the upper limit for the positive values and to the lower limit for the negative values. For example, parameter A has a positive mean-effect value of 0.356 and hence to reach the optimum its value must be shifted to its upper limit. On the contrary, parameter B has a negative mean-effect value of −0.259 suggesting that it should be shifted to the lower limit. Other parameters are accordingly adjusted during the design.

Keeping the above considerations in view, a total of three typical electrodes were fabricated with the values of parameters A to G given in Table 4. The analysis indicates that the electrode labelled as E_{18} has the optimum values of these parameters.

After optimizing the parameters A to G the elec-

Table 3. Yates' analysis of the data on bare-carbon electrodes for oxygen reduction in 1 M *KOH at 30° C*

Electrode No. (trials)	*Results (average potentials vs Hg/HgO, OH^- at 40 mA cm^{-2} load)* (V)	I	II	III	IV	*Mean effect* (IV)/8	*Factor/interaction responsible*	*Mean square = sum of squares* = $(IV)^2/16$
E_{15}	−0.240	−0.455	−1.691	−2.948	−6.226	−0.778	–	–
E_2	−0.215	−1.236	−1.257	−3.278	0.694	0.086	D	0.0301
E_3	−1.020	−0.747	−1.480	0.402	−0.066	−0.008	E	0.0003
E_{14}	−0.216	−0.510	−1.798	0.292	−0.106	−0.013	DE	0.0007
E_5	−0.215	−0.540	0.829	−0.544	0.116	0.014	F	0.0008
E_{12}	−0.532	−0.940	−0.427	0.478	0.336	0.042	AG=DF	0.007
E_{10}	−0.200	−1.338	−0.650	0.986	2.296	0.287	AB=EF	0.3295
E_8	−0.310	−0.460	0.942	−1.092	−0.964	−0.120	C≈DEF	0.0581
E_9	−0.195	0.025	−0.781	0.434	−0.330	−0.041	G	0.0068
E_7	−0.345	0.804	0.237	−0.318	−0.110	−0.013	DG	0.0007
E_6	−0.220	−0.317	−0.400	−1.256	1.022	0.127	EG	0.0653
E_{11}	−0.720	−0.110	0.878	1.592	−2.078	−0.259	B=DEG	0.2699
E_4	−1.090	−0.150	0.779	1.018	−0.752	−0.094	AD=FG	0.0353
E_{13}	−0.248	−0.500	0.207	1.278	2.848	0.356	A=DFG	0.5069
E_{16}	−0.280	0.842	−0.350	−0.572	0.260	0.032	EFG=ABG	0.0042
E_1	−0.180	0.100	−0.742	−0.392	0.180	0.022	AE=CG=DEFG	0.002
Total	−6.226							1.3176

$$\textit{Corrected sum of squares} = (-0.240)^2 + (-0.215)^2 + \ldots + (-0.180)^2 - \frac{(-6.226)^2}{16}$$

$$= 3.7405 - 2.4227$$

$$= 1.3178$$

Table 4. Final design of the bare-carbon electrodes from Table 3

Electrode No. (trials)	A (wt %)	B (wt %)	C (sec)	D (K)	E ($kg\,m^{-2}$)	F (sec)	G ($N\,m^{-2}$)	*Average potentials vs Hg/HgO, OH^- (1 M KOH) at 100 mA cm^{-2}* (V)
E_{17}	64	22.76	2580	400	500 000	300	4532	−0.181
E_{18}	68	21.52	2520	401	500 000	300	4398	−0.168
E_{19}	72	20.28	2400	402	500 000	300	4265	−0.187

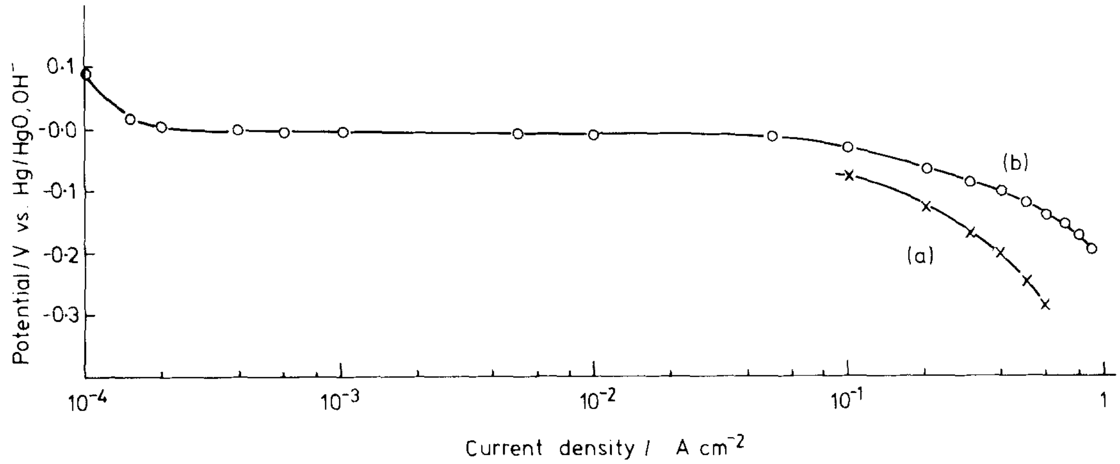

Fig. 1. Electro-reduction of oxygen in 6 M KOH electrolyte at 30° C on E_{18} electrode (a) with 7 wt % Pt [6] and (b) with 4 wt % Pt + 6 wt % Ru.

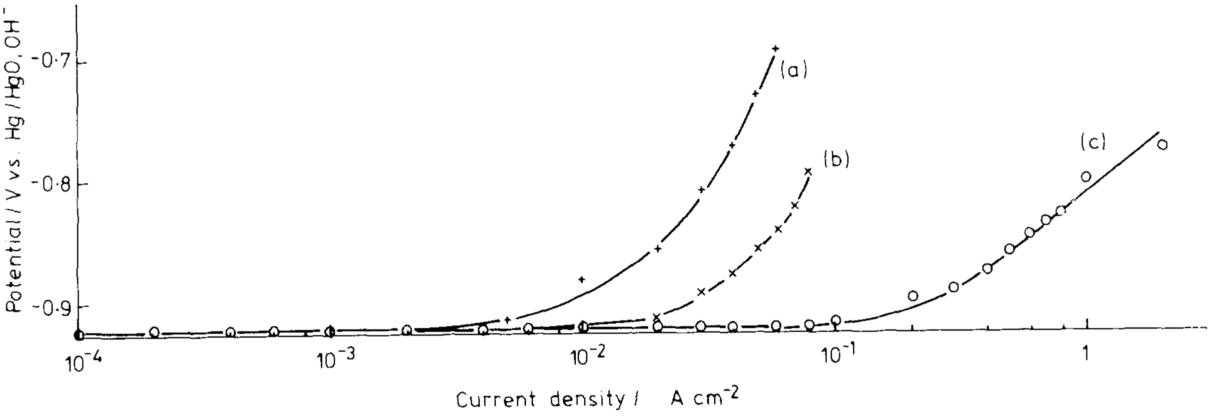

Fig. 2. Electro-oxidation of hydrogen in 6 M KOH electrolyte on E_{18} electrode (a) with 10 wt % Ru at 30° C; (b) with 4 wt % Pt + 6 wt % Ru at 30° C and (c) with 4 wt % Pt + 6 wt % Ru at 60° C.

trodes were coated with the catalyst. In this study, we have designed carbon electrodes containing a platinum-ruthenium bimetal catalyst by keeping the parameters *A* to *G* at optimum levels and varying the catalyst composition in a classical manner. Different compositions of the Pt-Ru catalyst were prepared by impregnating the carbon substrate with solutions of the respective salts (2 wt % H_2PtCl_6 an 1 wt % $RuCl_3$ in 2 M HCl) followed by reduction with 5 wt % sodium formate solution. The electrochemical data for such electrodes for reduction of oxygen as well as oxidation of hydrogen in 6 M KOH are shown in Figs 1 and 2 respectively; a comparison of this data with carbon electrode containing platinum is also included [6]. It is evident that by such a statistical design it is possible to fabricate electrodes with improved features.

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