



Parametric study of the preparation of gas-diffusion electrodes for alkaline fuel cells by a filtration method

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Abstract

The effects of various parameters in preparing Raney–Ni/PTFE anodes for alkaline fuel-cells are investigated. A partial factorial experiment design (2^{5-1}) analysis reveals that the important parameters are PTFE content and milling time, and their interaction. Thus, one parameter at a time is varied to study its effect on electrode performance. Electrodes prepared with 8 wt.% PTFE and with milling for 60 s exhibit the best performance. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

There are essentially two methods of making single-layered PTFE-bonded gas diffusion electrodes, namely: the ‘wet method’ and the ‘dry method’. In the wet method, the catalyst powder is blended with a PTFE suspension to make a dough, which is rolled using a heavy metallic cylinder. The dry method, which was proposed by Sauer [1] and improved by Winsel [2] and Winsel et al. [3], uses PTFE powder. Since both these techniques have certain drawbacks, the filtration method has been proposed and tested [4,5]. During the preliminary experiments of preparing Raney–Ni/PTFE electrodes with the filtration method, it was observed that variations in different parameters affect the electrode performance significantly. For example, the electrode overpotential at a given current density depends on the following parameters: (i) catalyst loading: total mass of the catalyst per unit geometric area of the electrode; (ii) PTFE content: wt.% of PTFE in the electrode; (iii) milling time: time period for which the catalyst and PTFE are milled; (iv) cooling (on/off): whether the catalyst is cooled during milling; (v) type of surfactant; (vi) amount of surfactant per unit volume of the slurry; (vii) vacuum applied during filtration; (viii) clearance of

the rolls: distance between the rolls of the calendar at second rolling of the electrode; (ix) removal of the surfactant: number of times surfactant is removed from the finished electrode by boiling acetone; (x) activation time: period during which the cathodic current is passed in the presence of hydrogen into the electrode for activation; (xi) activation temperature; (xii) electrolyte concentration; (xiii) temperature of the polarization; and (xiv) reactant gas pressure.

The first nine of these parameters are associated with electrode preparation while the remaining parameters belong to the performance evaluation. Five preparation parameters, namely, PTFE content, milling time, cooling while milling, roll clearance and surfactant removal are considered here in a statistical analysis. Their higher and lower level values are tabulated in Table 1. A 2^{5-1} design is used to determine significant parameters and to keep the numbers of runs reasonable. The effect of the significant parameters on electrode performance is studied experimentally by varying one at a time.

2. Experimental design

A full, 5-variable, factorial design of two levels will require 32 runs. In this study, lesser runs are required due to a limited mass of a batch of catalyst. A batch of conventionally passivated Raney–Ni [6] is approximately

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Table 1
Higher and lower levels of parameter values

	Parameters				
	A (PTFE content, wt.%)	B (Milling time, s)	C (Cooling, off/on)	D (Clearance, μm)	E (Number of removals)
Lower level (–)	8	30	Off	200	One
Higher level (+)	11	120	On	400	Three

300 g. It is necessary to make all electrodes in the same batch, as electrode performance also depends on the passivation. Since higher orders of parameter interactions are not important, a half-factorial design will not affect the result. Therefore, a 2^{5-1} partial factorial design, which needs only 16 runs, has been chosen. The construction of the design is shown in Table 2 by writing the 2^4 design in four parameters (*A*, *B*, *C* and *D*). Effect *E* column is found with generator $E = -ABCD$, which gives the defining relation for the design $I = -ABCDE$. Here, every main effect is aliased with a 4-factor interaction. All 2-effect interactions are aliased with 3-effect interactions. This approach is a V resolution design. Due to high resolution, it is expected that this design will provide relevant information about the main effects and second-order interactions [7].

3. Experimental

Hydrogen anodes (Ni/PTFE) for alkaline fuel cells were made by using the filtration method that has been explained elsewhere [4,5]. Raney–Ni was used as the electrocatalyst. It was made from Ni–Al alloy (Art. 806749, Merck) whose properties are listed in Table 3. Other materials were Ni mesh (99.9 wt.%, 0.5 mm \times D 0.14 mm), polytetrafluoroethylene powder (Hastafion TF 2053,

Table 2
Construction of 2^{5-1} factorial design and experimental results

Run no.	Parameters					Response variables (overpotential, mV)	
	A	B	C	D	E	at 100 mA cm ⁻²	at 150 mA cm ⁻²
1	–	–	–	–	+	145	203
2	+	–	–	–	–	123	185
3	–	+	–	–	–	161	242
4	+	+	–	–	+	139	209
5	–	–	+	–	–	148	222
6	+	–	+	–	+	128	192
7	–	+	+	–	+	172	258
8	+	+	+	–	–	130	195
9	–	–	–	+	–	152	228
10	+	–	–	+	+	121	182
11	–	+	–	+	+	155	233
12	+	+	–	+	–	126	189
13	–	–	+	+	+	160	240
14	+	–	+	+	–	143	215
15	–	+	+	+	–	166	249
16	+	+	+	+	+	129	194

Hoechst) and surfactant Brij 96 (polyoxyethylene{10} oyl ether, BDH).

A number of electrodes were made according to the experimental design and the polarization was measured in a half cell with 25 wt.% KOH electrolyte. A circular electrode sample of 6 cm² area was fitted in a Plexi-Glass holder. The holder has a gas chamber into which hydrogen gas enters at 6 psig. A nickel foil served as a counter electrode. The reference electrode was a commercially available Hg/HgO electrode filled with the 25 wt.% KOH solution. Electrochemical measurements were performed with Model-273A unit manufactured by EG&G Princeton Applied Research, Princeton, NJ, USA.

The passivated electrode was activated by applying a cathodic current density of 4.2 mA cm⁻² to the working electrode at 65°C for 25 h. The polarization data of the activated electrodes in the half-cell assembly were obtained galvanostatically for anodic current densities between 0 and 166.67 mA cm⁻² at 25°C.

4. Results and discussion

4.1. Analysis of the experimental design results

The IR-free overpotentials with respect to a Hg/HgO reference electrode at a temperature of 298 K and current densities of 100 and 150 mA cm⁻² are listed in Table 2. The statistical analyses were performed by Statgraphics, a software developed by the Statistical Graphics, USA [8]. The estimated effects and analysis of variance (ANOVA) are shown in Table 4. All 2-effect interactions that involve roll clearance (*D*) and surfactant removal (*E*) are eliminated as being physically insignificant. From the tabulated results, it is concluded that the important variables are

Table 3
Properties of Raney–Ni alloy

Chemical composition	
Ni content	50.0 wt.%
Al content	50.0 wt.%
Solid phase density	4.1 g cm ⁻³
Particle density	3.99 g cm ⁻³
Porosity	0.027
Pore volume	0.007 cm ³ g ⁻¹

Table 4
Analysis of variance and estimated effects

Effects	Sum of squares	DF	Mean square	F-ratio	P-value	Estimated effects
<i>Analysis for 150 mA / cm⁻²</i>						
A: PTFE	6162.25	1	6162.25	38.07	0.0005	-39.25
B: Milling time	650.25	1	650.25	4.02	0.0851	-12.75
C: Cooling	552.25	1	552.25	3.41	0.1072	11.75
D: Clearance	36	1	36	0.22	0.6564	3.0
E: Removal	12.25	1	12.25	0.08	0.794	1.75
AB	361	1	361	2.23	0.179	-9.5
AC	64	1	64	0.4	0.5559	-4.0
BC	144	1	144	0.89	0.3867	-6.0
Total error	1133	7	161.8571			
Total	9115	15				
<i>Analysis for 100 mA / cm⁻²</i>						
A: PTFE	3025	1	3025	46.98	0.0002	-27.5
B: Millings time	210.25	1	210.25	3.27	0.1137	-7.25
C: Cooling	182.25	1	182.25	2.83	0.1364	6.75
D: Clearance	2.25	1	2.25	0.03	0.8589	0.75
E: Removal	0	1	0	0	1	0
AB	100	1	100	1.55	0.2528	-5
AC	9	1	9	0.14	0.7234	-1.1
BC	30.25	1	30.25	0.47	0.5222	-2.75
Total error	450.75	7	64.3929			
Total	4009.75	15				

PTFE content (A), milling time (B), the cooling (C), and the interaction of A and B.

4.2. Reactive mixing

Reactive mixing, which is the high-speed milling of catalyst with PTFE particles, is the main step of the filtration and the dry methods. The amorphous PTFE particles have some cracks and range between 20 to 600 μm in size, as evident from the electron micrograph shown in Fig. 1a.

When these particles are milled with Raney-Ni, they fragment into sub-micron pieces. The fragmented pieces adhere on the catalyst surface as shown in the electron micrograph presented in Fig. 1b. These fine fragments work as a binder, when certain pressure is applied to the milled powder. In addition, the PTFE fines on the catalyst surface bestow the required hydrophobicity. The micropores are still hydrophilic because PTFE does not enter into them. When an electrode made with the milled particles is dipped into the electrolyte, only a very small quantity of the electrolyte can stay in the spaces between the catalyst particles and allow reactant gas to diffuse. Nevertheless, the electrolyte can infuse into the microporous structure of individual particles by capillary action, and flood them.

4.3. Effect of main parameters on the electrode performance

The effect of the important parameters on the electrode performance is studied in detail. Each parameter is varied

while keeping other parameters at a predetermined base value. The base values of these parameters are given in Table 5.

4.3.1. PTFE content

Different electrodes were made with 1, 2, 5, 8, 11 and 14 wt.% PTFE. The overpotential at 100 mA cm^{-2} is plotted against the PTFE content in Fig. 2. The overpotential first decreases with increasing PTFE content and reaches a minimum at 8 wt.%. Then, the overpotential increases at a slower rate. This behaviour is in agreement with the optimum value for the wet method electrodes obtained by Jenseit et al. [9]. The variation in overpotential with PTFE content is explained in terms of the schematic diagram shown in Fig. 3. The higher overpotential of electrodes with less PTFE is mainly due to poor binding and lack of hydrophobicity of the catalyst particles. It was observed that the electrodes were fragile at 1 and 2 wt.% PTFE. Apparently, lack of hydrophobicity permits the ingress of electrolyte into the external pores, as shown in Fig. 3a, and thereby results in slower gas diffusion. This additional diffusional resistance translates into a higher electrode overpotential. At the optimum PTFE content, the PTFE fragments cover a partial external area of the catalyst particles so that introduction of the electrolyte into the micropores is facilitated. The external surface of the particle is hydrophobic. Therefore, the macropores are largely free from electrolyte as indicated in Fig. 3b. When the PTFE content exceeds the optimum value, the uncovered area starts to decrease. Consequently, a few micropores are

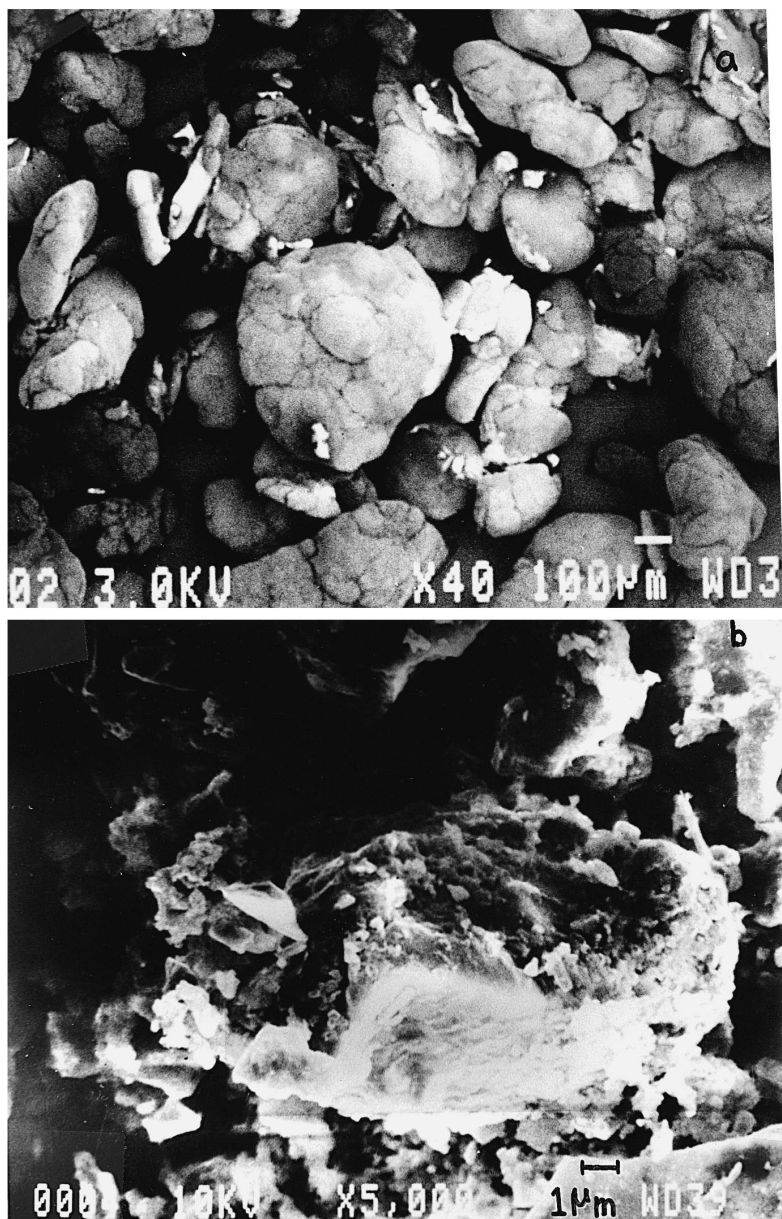


Fig. 1. Scanning electron micrographs of (a) PTFE particles, and (b) milled Raney-Ni catalyst.

Table 5

Base values of various electrode preparation parameters

Parameters	Value
PTFE content	8 wt.%
Milling time	60 s
Cooling	On
Clearance between rolls	400 μm
Surfactant removal	Once
Activation time	25 h
Activation temperature	65°C
KOH concentration	25 wt.%
Polarization temperature	25°C
Gas pressure	6 psig
Catalyst loading	120 mg cm^{-2}
Filtration vacuum	300/500 mbar

rendered empty (cf. Fig. 3c). Due to the blockage of the micropore openings, gas diffusion is also restricted.

4.3.2. Milling time

The polarization data were obtained for electrodes using catalyst milled for 30, 60, 90, 120, 150 and 200 s. The overpotential at 100 mA cm^{-2} is plotted against milling time in Fig. 4. Two sets of data were obtained to establish reproducibility. The overpotential of the electrode made with catalyst milled for 30 s is relatively high, then comes to a minimum at 60 s. There is little variation in the overpotential when the catalyst is milled for more than 120 s. For a short milling time, all the PTFE particles apparently do not have the chance to fragment completely into

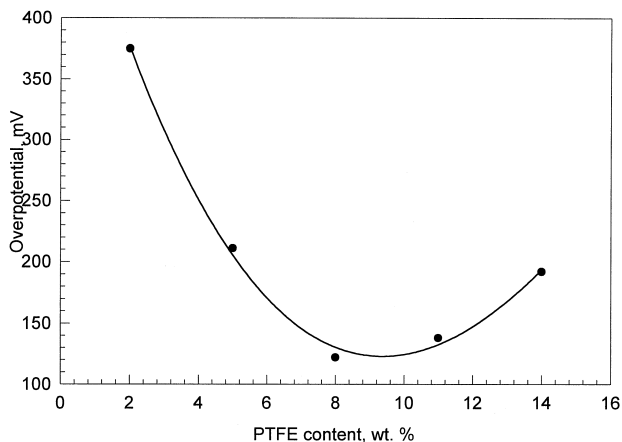


Fig. 2. Electrode overpotential at 100 mA cm^{-2} vs. PTFE content.

small fines and adhere on the catalyst particles. This inadequate PTFE coating results into poor binding and lack of hydrophobicity. The electrolyte has a chance to fill external pores (cf. Fig. 3a) and promote a diffusion resistance. At optimum milling time, the hydrophobicity is such that most of the external pores are empty and are available for gas diffusion. When milling is performed for longer periods, the PTFE particles become fine. The friction among the catalyst particles generates heat that assists in the coating of the catalyst. Consequently, a considerable external area of catalyst is covered. This increases the hydrophobicity of the particles and blocks micropore openings at the external surface. As a result, microporous diffusion becomes difficult despite the availability of gas in the macropores. After a certain milling time, the rise in the overpotential is not appreciable. This is because further coating is unlikely due to limited PTFE.

4.3.3. Cooling while milling

If the heat generated by milling is not removed, the PTFE fines tend to coat the catalyst particles and cause

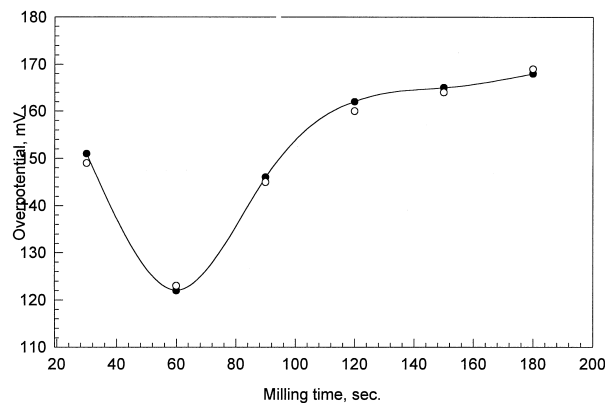


Fig. 4. Electrode overpotential at 100 mA cm^{-2} vs. milling time.

blockage of the micropore openings at the external surface area. The effect is much more pronounced when milling is undertaken for long periods. On the other hand, when the generated heat is removed continuously by circulating cold water, excessive covering of the catalyst particles is unlikely. This is the reason for observing a marginally higher overpotential when cooling was not applied. The polarization curves of the electrodes produced with 60 s milling, 8 wt.% PTFE and $400 \mu\text{m}$ clearance are shown in Fig. 5. The overpotentials of the electrode that used catalyst milled without cooling are slightly higher.

4.3.4. Removal of the surfactant

The polarization curves shown in Fig. 6 were obtained from two samples of one electrode. One sample was washed with boiling acetone for 5 min, while the other was not treated in this way. The latter sample displays unusually high overpotentials. It can be inferred, therefore, that the removal of the surfactant is extremely important. It is hypothesized that the surfactant adheres on the catalyst surface. This prohibits the reactant gas from reaching the active sites. Due to this blockage, the electrode perfor-

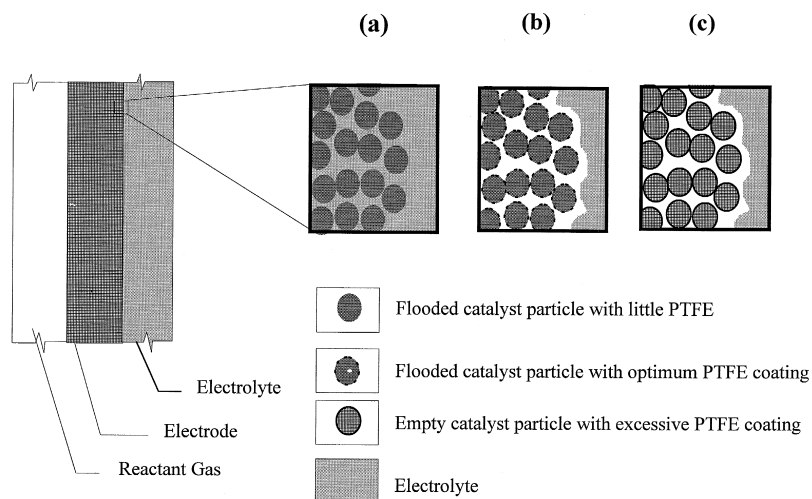


Fig. 3. Schematic diagram of catalyst particle in an electrode with: (a) little, (b) optimum, and (c) excessive PTFE coating.

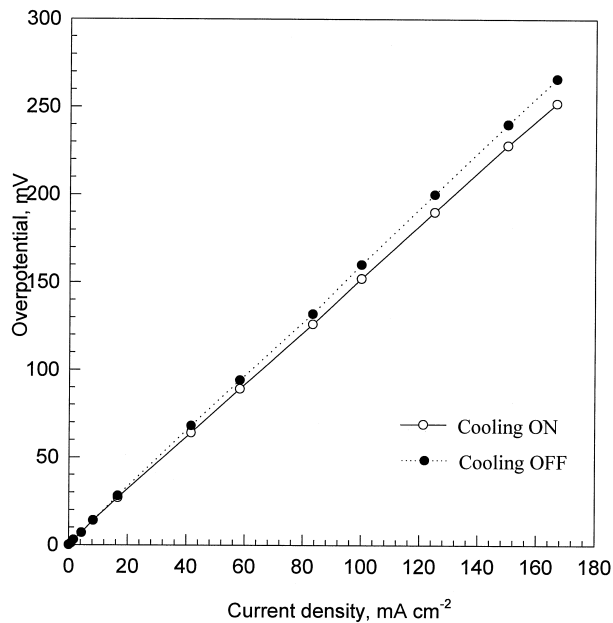


Fig. 5. Polarization of electrodes prepared with catalyst milled while cooling was either on or off.

mance drastically drops. Although the removal of the surfactant is extremely important, the results of partial factorial design show that removing it once is sufficient.

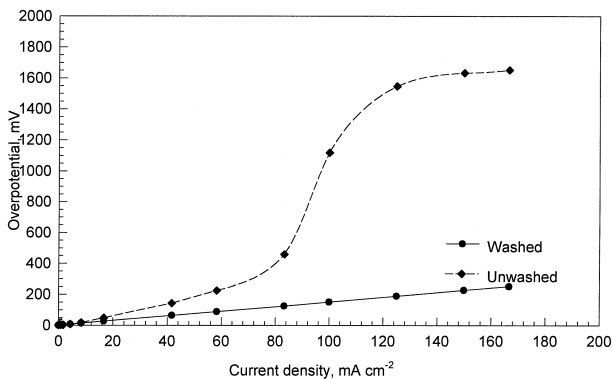


Fig. 6. Electrode polarization with and without acetone washing.

5. Conclusions

The significant parameters in the preparation of gas diffusion electrodes are PTFE content, milling time, cooling while reactive mixing, and the interaction of PTFE content and milling time. To obtain the best performance, the PTFE content and milling time should be 8 wt.% and 60 s, respectively, and cooling must be applied. Notwithstanding that these conclusions are specific to Raney–Ni gas diffusion electrodes for alkaline fuel cells, the results can be generalized for any electrode with a hydrophillic catalyst and a hydrophobic binder.

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