

Preparation of Raney–Ni gas diffusion electrode by filtration method for alkaline fuel cells

SLEEM-UR-RAHMAN, M. A. AL-SALEH*, A. S. AL-ZAKRI, S. GULTEKIN

Department of Chemical Engineering, King Fahd University of Petroleum and Minerals, Dhahran-31261, Kingdom of Saudi Arabia

Received 17 October 1995; revised 3 June 1996

A novel filtration method for preparation of gas diffusion electrodes for fuel cells is proposed. This method, which is a modification of the conventional dry method, has the merits of both wet and dry techniques. The electrode performance is improved due to better structure, controlled hydrophobicity and less compaction. To compare the effectiveness of the method, Raney–Ni/PTFE anodes for use in a KOH fuel cell were made. Their electrochemical performance was compared with similar electrodes produced by the dry method by other research groups, under the same conditions. The filtration method electrodes performed better between temperatures of 25 °C and 75 °C. The electrode exhibited no significant degradation of activity in the first 180 h at 100 mA cm⁻² anodic load.

1. Introduction

The performance of fuel cell electrodes can be improved by either using a more active electrocatalyst or by improving its structure in order to minimize transport losses and to increase the chances of simultaneous contact of gaseous reactant, catalyst and electrolyte [1]. There are essentially two methods of making single-layered PTFE–bonded Raney–Ni gas diffusion electrodes, namely; the wet method and the dry method. In the wet method, the catalyst powder is blended with aqueous PTFE suspension, to make a dough which is processed further. The dry method was proposed by Sauer [2] and improved by Winsel [3, 4]. In this method the passivated catalyst is knife-milled with PTFE powder. In this process PTFE particles fragment into tiny filaments, which partially coat the catalyst particles. Cooling of the catalyst while milling further assists in this process [5]. As a result of the process which is known as ‘reactive mixing’, a fluffy mass of the powder is produced. This fluffy powder is rolled to obtain a catalyst tape. In a subsequent step the catalyst tape is rolled with a nickel screen which acts as current collector and provides mechanical strength. This method has the following disadvantages:

- (i) While rolling the dry powder, a high rolling pressure is required which results in higher diaphragm resistance and builds up a diffusion barrier for the reactant gas [6].
- (ii) Powder rolling is not well understood.
- (iii) Control on the flow rate of the powder into nip of the rolls is difficult and subjective. The varying flow rate results in uneven electrode morphology.
- (iv) Rolling of the powder can take place successfully in a narrow range of the parameters. As con-

straints on the parameters are increased optimization becomes difficult.

- (v) Reproducibility is not ensured as uncontrollable variables come into the picture.
- (vi) Loss of catalyst occurs.

Electrodes made according to the dry method are thin (200–400 μm) and inexpensive because PTFE emulsion is not used. However, the activity of the electrodes is somewhat lower than of those made by the wet method [7]. As both methods use the same catalyst, any difference in the effective activity is due to the structure of the electrode. In this work a novel method, called the ‘filtration method’, is introduced which eliminates the problem of the structure to a certain extent.

The proposed method is a modification of the dry method. Until the fluffy powder of catalyst and PTFE from the reactive mixing is produced the steps are similar to those of dry method. Instead of making the catalyst tape by cold rolling of the dry powder, a slurry of the milled catalyst is made using a suitable surfactant. The slurry is filtered on a filter paper by the application of regulated vacuum to form a uniform filter cake. The filter cake with the filter paper is air dried and rolled with the nickel screen. In this step the catalyst web is transferred to the nickel mesh from the filter paper. A small amount of surfactant is present in the electrode which is removed by boiling in acetone. This method has the following advantages:

- (i) Uniformity in the thickness of the electrode is ensured.
- (ii) Macroporosity of the electrode can be controlled.

*To whom correspondence should be addressed

Table 1. Properties of Raney-Ni alloy and catalyst

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

- (iii) High compaction pressure is not required therefore the diaphragm resistance in the electrode is low.
- (iv) Preparation parameters (e.g., PTFE content) can be varied over a wider range.
- (v) Mass production of the electrodes is possible and can be controlled.
- (vi) Filtration is a well understood process.

2. Experimental details

2.1. Materials

Raney-Ni catalyst is the main material used in the electrode preparation. It is made from Ni-Al alloy (Art. 806749, Merck) whose properties are listed in Table 1. Other materials are Ni mesh (99.9 wt%, 0.5 mm × D 0.14 mm), Polytetrafluoroethylene powder (Hastafion TF 2053, Hoechst) and surfactant Brij 96 (Polyoxyethylene{10}olyl ether, BDH).

2.2. Electrode preparation

The main experimental parts of the electrode preparation by the filtration method as detailed in Fig. 1, consist of catalyst preparation, reactive mix-

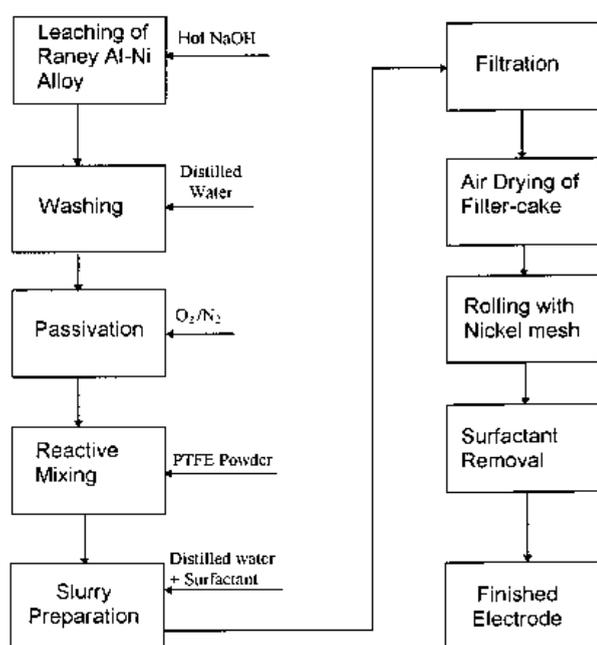


Fig. 1. Flow diagram for electrode preparation by filtration method.

ing, preparation of slurry, formation of filter cake, cold rolling and finally removal of surfactant traces.

2.2.1. Catalyst preparation. The finely ground powder of Ni-Al alloy is leached by using a 25% NaOH solution. The leaching parameters were chosen on the basis of the experimental study of Choudhary *et al.* [8]. From this, a fine black pyrophoric powder is produced which is washed several times with distilled water to remove the aluminium salts which may plug the porous structure of the catalyst. The washing is stopped when the pH has reached neutral. The catalyst is highly pyrophoric and therefore has to be passivated before making the electrodes. The passivation is done by controlled oxidation of the catalyst. A known mass of washed catalyst, which is still wet, is placed into a vacuum oven. The catalyst is heated for several hours at 40 °C and 300 mbar. Once the catalyst powder looks dry, a small dose of oxygen is introduced into the oven until the pressure is 400 mbar. While doing this, the temperature of the catalyst is observed carefully. If the temperature rises sharply nitrogen gas is purged into the oven. After waiting approximately half an hour, this process is repeated. The introduction of small doses is continued until atmospheric pressure is reached. A small sample of dry catalyst is kept in a watch glass and observed carefully. If the catalyst is successfully passivated, no visual burning should occur. Before using this catalyst, it is characterized using BET surface area measurement, Hg intrusion porosimetry, X-ray diffraction and scanning electron microscopy. The BET surface and average particle size of the batch used were 72 m² g⁻¹ and 25 μm, respectively.

2.2.2. Reactive mixing with the PTFE. PTFE is mixed with the catalyst by a method known as reactive mixing proposed by Winsel *et al.* [4]. A predetermined quantity of PTFE is blended with the catalyst with a glass rod until the PTFE particles apparently disappear. This mixture is transferred into a special high speed grinder (speed 20 000 rpm, type M-20, Jankel and Kunel GmbH) which has two sharp knives and provision for cooling the catalyst. The catalyst is milled in this grinder for a required period. While milling, the mixer is vigorously tumbled to avoid dead zones in the mixer.

2.2.3. Preparation of slurry. For making the slurry, the selection of surfactant is most important. A very stable suspension is not required, as the main function of the surfactant is wetting. The surfactant must not generate too much foam, as this affects the formation of the filter cake. Considering these requirements, Brij-96 was selected. A predetermined quantity of milled catalyst required for the desired catalyst loading (e.g., 10.3 g in 500 ml distilled water for 100 mg cm⁻² loading) is transferred to the mixer. Before pouring the water into the mixer, surfactant is added. This mixture is blended until visual dispersion is achieved.

2.2.4. Formation of the filter-cake. Filtration is used to form a uniform filter-cake of catalyst to obtain a uniform electrode. This is done in a vacuum filtration apparatus by using a Whatman filter paper no. 42. A Buchner funnel is mounted on a conical flask which is connected to a vacuum pump via a vacuum regulator. The catalyst slurry is decanted into the Buchner funnel at which the vacuum is maintained at 500 mbar. The vacuum is changed to 300 mbar. At this vacuum level, all of the slurry water is allowed to filter out. Consequently, a uniform filter cake is formed on the filter paper. The filter cake with the filter paper is removed and allowed to dry in air for 2 h. Special care must be taken while handling this cake because it is fragile as the catalyst particles has not formed bonds.

2.2.5. Cold rolling. A precut and prerolled metallic mesh is placed over the air dried filter cake while a filter paper is placed over the metallic mesh. This whole assembly is rolled at room temperature in a rolling machine at a desired clearance. The filter papers from the rolled assembly are removed leaving the catalyst web on the mesh. This web with the mesh is rolled again without filter paper to provide strength while maintaining a clearance which must be less than that of the first rolling. The macroporosity of the electrode may be controlled in this step by varying the clearance. It is imperative to remove the remaining surfactant. Through some preliminary trials, it was found that the surfactant is soluble in acetone. Therefore, the freshly made electrode is boiled in acetone for 5 min to remove the surfactant.

2.3. Electrode performance

The electrodes produced by the filtration method were investigated in a half-cell setup. A circular electrode sample of 6 cm² area was fitted in a Plexi-glass holder. The holder had a gas chamber with inlet and outlet for reactant gas entering via a pressure regulator and pressure indicator. A nickel foil served as a counter electrode. The reference electrode was a commercially available Hg/HgO electrode filled with the 25% KOH solution. A 25 wt% KOH solution was used as electrolyte. The potentiostat was model-273A manufactured by EG&G PARC. The equipment had an in-built IR compensation facility using two methods; positive feedback and current interruption.

The passivated electrode was activated by applying a cathodic current density of 4.2 mA cm⁻² to the working electrode at 60 °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 to 166.67 mA cm⁻². Ten minutes after changing the current density, the electrode potential became steady. The electrolyte temperature was varied between 25 °C and 75 °C.

3. Result and discussion

After several preliminary runs, a representative Ni/PTFE electrode was produced by the new method. This electrode had 8.0% PTFE, 100 mg cm⁻² nickel loading and a thickness of 400 μm. The polarization of this electrode was measured at different temperatures (25–75 °C) and compared with similar Raney-Ni/PTFE electrodes (8% PTFE and 100 mg cm⁻² loading) prepared by the dry method at DLR, Germany and studied by Celiker [9]. The polarization data at different temperatures are plotted in Figs 2 and 3. At all testing temperatures the overpotential for the filtration method were lower than those for dry method. These experimental data were used with the mathematical model developed by the authors [10] to obtain exchange current densities. These values, as indicated in Table 2, are higher for the filtration method. The exchange current density is temperature dependent. An Arrhenius type of plot yields an apparent activation energy of 75.9 kJ mol⁻¹ whereas this value is 73.9 kJ mol⁻¹ for the dry method. As the catalyst used in both methods is the same, the improvement in the performance is essentially due to the improved structure of the electrode.

The reactive mixing is the most important step in both methods. The dry PTFE powder consists of amorphous particles of size ranging between 20 μm to 600 μm. As evident from the SEM in Fig. 4 the particles have cracks. When these particles are milled together with metallic catalyst powder, they fragment into small pieces of less than 1 μm. The fragmentation of these particles may take place in two ways. First, the particles come in contact with the sharp knives of the mill rotating at high speed. Secondly, the metallic catalyst particles, which are moving at high speed, apply shear forces to the PTFE particles. During this process considerable heat is generated. This heat softens the PTFE particles facilitating their adherence at the external surface of the catalyst particles as shown in SEM in Fig. 5. These fine fragments act as binder when a certain pressure is applied to the milled powder. The PTFE fines on the catalyst surface provide the required hydrophobicity. When an electrode made with the milled particles is dipped into the electrolyte, only a very small quantity of the electrolyte stays in the space between the catalyst particles. This space is therefore available to reactant gas diffusion. However, the electrolyte can

Table 2. Exchange current densities at different temperatures

Temp. °C	Exchange current density, 10 ⁶ i ₀ /mA cm ⁻²	
	Dry method	Filtration method
25	11	24
35	26	66
45	85	164
55	160	378
65	300	836
75	1000	1763

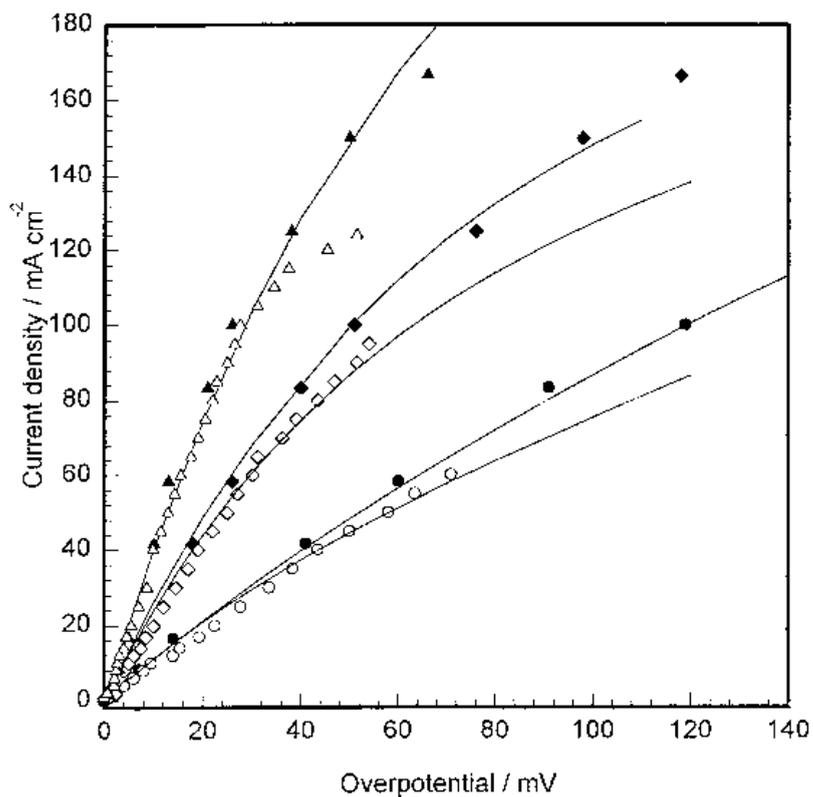


Fig. 2 Polarization of electrodes prepared by dry and filtration methods at 25, 45 and 65°C in 25 wt% KOH. Key: (—) model; (●) filtration at 25°C, (◆) filtration at 45°C, (▲) filtration at 65°C, (○) dry at 25°C, (◇) dry at 45°C, (△) dry at 65°C.

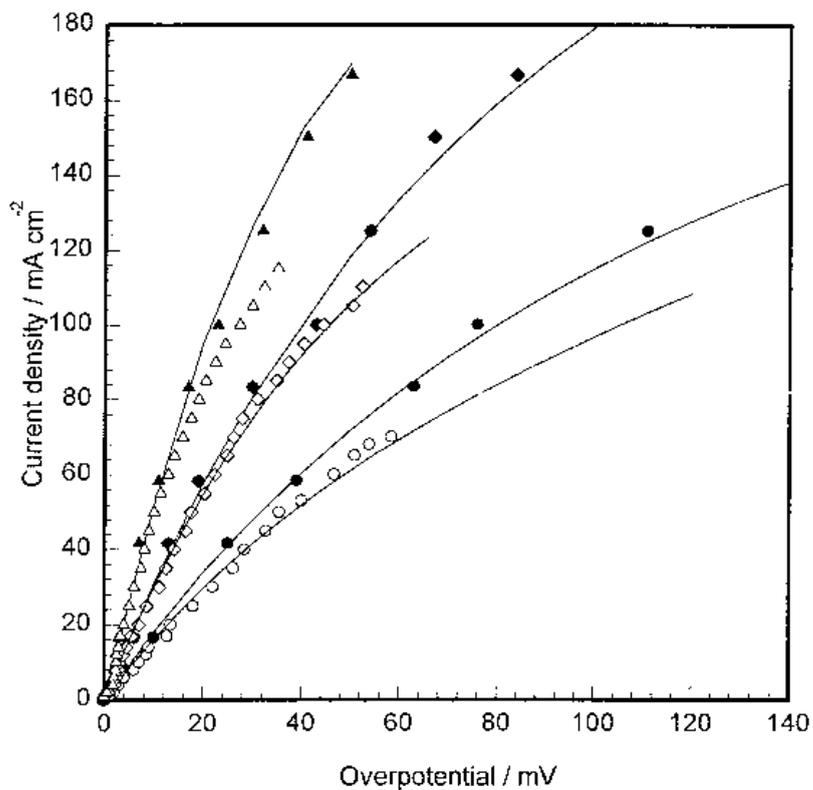


Fig. 3. Polarization of electrodes prepared by dry and filtration methods at 35, 55 and 75°C in 25 wt% KOH. Key: (—) model; (●) filtration at 35°C, (◆) filtration at 55°C, (▲) filtration at 75°C, (○) dry at 35°C, (◇) dry at 55°C, (△) dry at 75°C.

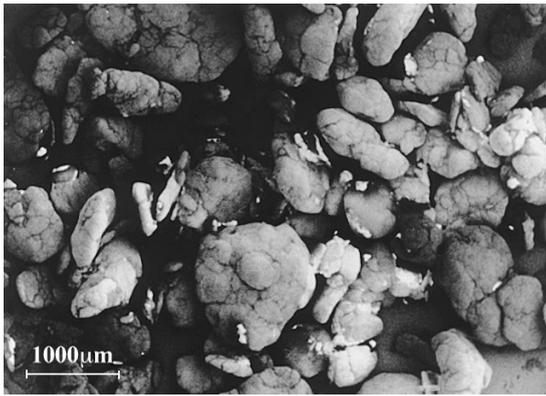


Fig. 4. SEM micrograph of PTFE particles.

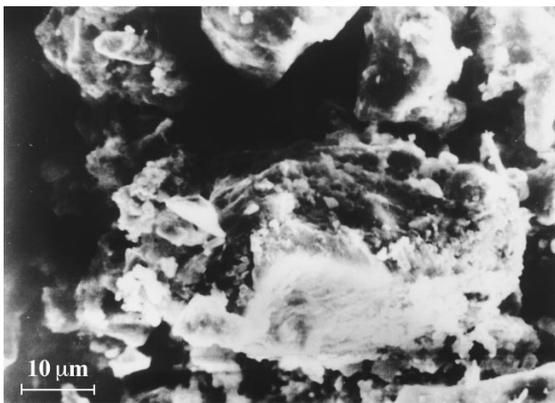


Fig. 5. SEM micrograph of milled Raney-Ni / PTFE.

enter the microporous structure of the individual particle and cause flooding. Electrolyte flooding is basically due to capillary action. As PTFE does not enter the micropores, they are still hydrophilic and assist in electrolyte flooding. These micropores filled with electrolyte work as immobilized phase. The actual electrochemical reaction takes place on the catalyst surface of the micropores in the presence of electrolyte and diffused reactant gas.

By the wet method, uniform electrodes can be formed with greater ease. But controlling the hydrophobicity and obtaining a favourable electrode structure is difficult. This is because the PTFE par-

ticles have little chance to adhere to the surface of the catalyst. Instead, the particles remain as such amongst the catalyst. On the other hand, in the dry method, although the adherence of PTFE particles is good, due to reactive mixing, excessive pressures applied for dry rolling of the powder into a uniform tape compacts the electrode. High rolling pressure and stress induce a layered structure. This may increase the diaphragm resistance[7] and, additionally, may build up a diffusion barrier for the reactant and products.

In the filtration method electrodes are rolled with relatively lower pressure. Therefore, the gaseous diffusional resistance is reduced. Moreover, the controlled hydrophobicity of the particles allows more inter-particle space or macropores to be empty. As diffusional resistance in the electrolyte is much higher than in the empty pores, the overall resistance is further reduced. Thus, the new method has the merits of both conventional methods (i.e., controlled hydrophobicity, lesser compaction and easy formation). This method allows better control of the porosity of the electrode. This can be done by varying the pressure in the final rolling of the electrode. The PTFE content can be varied over a wider range unlike the dry method as a minimum PTFE content is required for dry rolling. In addition to these advantages the loss of catalyst is low as the filter cake can be made of any desired shape and size.

The electrode made by filtration method was subjected to a constant anodic load of 100 mA cm^{-2} at 25°C . The potential change with respect to time was recorded. As depicted in Fig. 6. The electrode potential remained almost constant for 180 h. The test was discontinued due to the limited time. This result is encouraging but to establish the commercial utility of the electrode long term performance tests for more than 1000 h are required.

4. Conclusions

Raney-Ni gas diffusion electrodes for KOH fuel cells performed better when prepared by the proposed filtration method in comparison to similar electrodes made by a dry method under same testing conditions.

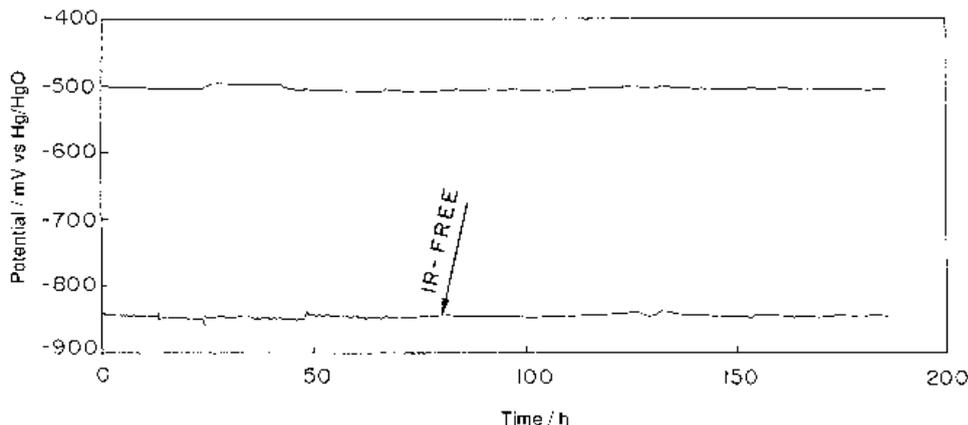


Fig. 6. Long term performance of the electrode under 100 mA cm^{-2} anodic load at 25°C .

The improvement in the electrode performance was essentially due to the improved structure of the electrode. The new method improves the structure of the electrode and has the merits of both conventional methods; that is, controlled hydrophobicity, lesser compaction and easy formation. Besides these advantages the new method minimizes wastage of catalyst and allows a wider range of preparation parameters and also affords the possibility of mass production.

Acknowledgements

Acknowledgement is due to the King Abdulaziz City for Science and Technology (KACST) for their financial support under HYSOLAR project. Thanks are also due to King Fahd University of Petroleum and Minerals for the use of their facilities.

References

- [1] H. A. Liebhafsky and E. J. Cairns, 'Fuel Cells and Fuel Batteries: A Guide to their Research and Development, Wiley, New York (1968).
- [2] H. Sauer, *German Patent D.E.-O.S. 2941774* (1979).
- [3] A. Winsel, *German Patent D.E.-O.S. 3710168* (1987).
- [4] A. Winsel, O. Fuhrer, K. Ruthling and C. Fischer, *Ber. Bunsenges. Phys. Chem.* **94** (1990) 926.
- [5] K. Bolvin, E. Gulzow and W. Schnurnberger, 'Fuel Cells Seminar Abstract', Long Beach, California (1988) p. 1964.
- [6] B. Kohler and A. Winsel, *Z. Naturforsch.* **19a** (1964) 602.
- [7] W. Jensiet, A. Khalil and H. Wendt, *J. Appl. Electrochem.* **20** (1990) 893.
- [8] V. R. Choudhary, S.K. Chaudhari, and A.K. Gokarn, *Ind. Eng. Chem. Res.* **28** (1989) 33.
- [9] H. Celiker, PhD dissertation, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia (1990).
- [10] M. A. Al-Saleh, S. Gultekin, Sleem-ur-Rahman and A. S. Al-Zakri, *J. Power Sources* **55** (1995) 43.