

A new immobilized-alkali H₂/O₂ fuel cell

S. Rowshanzamir¹, M. Kazemeini^{*}

Department of Chemical Engineering, Sharif University of Technology, PO Box 11365-9465, Azadi Ave., Tehran, Iran

Received 7 January 1999; received in revised form 29 October 1999; accepted 23 December 1999

Abstract

A new kind of fuel cell has been designed and constructed. This is called an immobilized-alkali H₂/O₂ single fuel cell, where the electrolyte is embedded in a porous matrix. Also, a different approach to electrode production for alkaline fuel cells is considered. Electrodes are single-layer, Teflon-bonded, gas-diffusion type and prepared by the pressing technique. Details of the preparation for these electrodes and their physical characterization by means of BET analysis, porosimetry, scanning electron microscopy and electrochemical evaluation (including Tafel and potentiostatic studies) are reported. The voltage–current behaviour of the fuel cell is determined under different operational conditions. The efficiency is 66% at a temperature of 25°C and a pressure of 1 bar. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Fuel cell; Immobilized-alkali; Design; Electrode preparation

1. Introduction

Fuel cells are the most efficient means of converting hydrogen to electric power, but are still a young technology. Many technical and engineering challenges remain. The most serious problem is that fuel cells are still too expensive. This is because insufficient members are being made to allow economies-of-scale.

Fuel cells are categorized by their most important component, namely, the electrolyte. This determines the operating temperature and catalyst utilized in the electrodes, as well as the process-gas requirements [1]. There are two types, i.e., polymer membrane, alkaline, phosphoric acid, molten carbonate, or solid oxide fuel cells [2]. The most researched is the hydrogen–oxygen system with an alkaline electrolyte. Such cells are under further development in many companies and research centres [3]. The systems that provide the highest power densities are the alkaline (AFC) and proton-exchange membrane (PEMFC) fuel cells [4].

The first operational alkaline fuel cell (6 kW) was built by F.T. Bacon in the 1950s. During the 1960s, Pratt and Whitney developed cells which were used in the first moon mission of the Apollo 8 space program. The alkaline fuel cell is currently considered by NASA to be the most reliable source of electricity for space shuttle travel operations. A major consideration is that AFCs are cheap in comparison with other small fuel cell systems [5,6].

In this paper, a detailed preparation technique for polytetrafluoroethylene (PTFE)-bonded gas-diffusion electrodes is presented. These electrodes were analyzed via porosimetry, BET surface-area measurements, scanning electron microscopy (SEM), Tafel and potentiostatic methods. Finally, the electrodes were incorporated in a research cell and the resulting behaviour was investigated.

2. Experimental

2.1. Electrode preparation

Basic components of a fuel cell are its electrodes (i.e., anode and cathode) and the electrolyte matrix layer. It should be mentioned that all structures and components within the fuel cell greatly influence the performance of electrodes. Therefore, to obtain a better performance, the

^{*} Corresponding author. Fax: +98-21-600-58-19.

E-mail address: kazemini@che.sharif.ac.ir (M. Kazemeini).

¹ Current address: Renewable Energy Group, Green Research Institute, The Iran University of Science and Technology, Tehran, Iran.

electrodes have to meet many partly divergent requirements [7], which include:

- mechanical stability under operational conditions
- electronic conductivity (i.e., electric contact surface)
- capacity of electrolyte absorption (i.e., hydrophilic micropores)
- transport paths for ions (i.e., low electrolytic resistive)
- porosity for gas diffusion (i.e., hydrophobic macropores)
- chemical stability against corrosion or oxidation.

In this work, the electrodes were made entirely of electrocatalysts and abricated by the 'dry' method, in which PTFE powder (Aldrich Chemical, USA) was used as a binder. The hydrogen electrode (i.e., the anode) was made of Raney nickel (Riedel-deHaen, Germany). In general, Raney metals are in a very finely divided, highly active form and are prepared by mixing the active with an inactive metal, usually aluminum. This intimate mixture, which is not a true alloy, is then treated with strong alkali to leach out the aluminum and leave a highly developed surface structure, which is required for the porous electrodes [8].

The anode is a PTFE-bonded Raney-Ni gas diffusion electrode with a Cu net, while the cathode is a PTFE-bonded Ag (99.95%, 30 mesh, Johnson Matthey Chemicals, England) gas-diffusion electrode with Ni-plated Cu net. The Cu net and Ni-plated Cu net act as current collectors and have a thickness of 0.2 mm. Because of the flammability of Raney Ni in air, the preparation of hydrogen electrodes were performed under a nitrogen atmosphere. The copper-impregnated, Raney Ni gas-diffusion electrode, gave better performance than the Raney Ni electrode. The lower polarization caused by Cu impregnation may be due to the fact that Cu decreases the contact resistance [10]. Thus, to achieve optimum performance copper oxide (Cu_2O , Riedel-deHaen, Germany) was added to the Raney Ni electrode.

To provide the necessary porosity for gas diffusion, filler materials (i.e., ammonium bicarbonate, Merck, Germany) were incorporated in the cathode electrode. The mixture was homogenized and then pressed into the current collector. The filler was then removed by drying at 100°C . A thin sheet of electrode (1 mm) was obtained. These electrodes had a circular shape and a geometric area of 37 cm^2 . The hydrogen electrode is highly active and, in

fact, is pyrophoric, i.e., it will catch fire in air when left dry. Consequently, it is necessary to store such electrodes in water after they have been prepared. Table 1 shows the composition of these electrodes.

2.2. Evaluation of electrodes

2.2.1. Physical characterization

Grain-size and pore-size distribution of the electrodes, as well as the average pore diameter were determined by means of an image analyzer (Q-570, Leica). The microstructure of both porous electrodes (i.e., anode and cathode) was examined with a scanning electron microscope (SEM, Stereo Scan Model S 360, Cambridge Instruments). Electron micrographs of the electrodes at various magnifications ranging from $\times 500$ to $\times 5000$ were obtained.

The specific surface area of the electrodes was measured with a BET surface area analyzer (Quantasorb), while a Porosimeter-2000 was used to determine the porosity.

2.2.2. Electrochemical characterization

Tafel and potentiostatic curves were obtained with an EG&G potentiostat/galvanostat unit (Model 273 A) which was controlled by an IBM PC/value point computer through 270/250 and 352 software in conjunction with a calomel reference electrode.

2.3. Fuel cell design

A single, hydrogen–oxygen fuel cell of the alkaline matrix type was designed and constructed. A schematic representation of this research cell is given in Fig. 1. The cell was fabricated from 316 stainless-steel and consisted of two cylindrical sections each with an inlet and outlet for gas supply and removal, and a volume of 120 cm^3 with an internal diameter of 75 mm. These two sections are sandwiched around the electrolyte, 30 wt.% KOH, which is embedded in 3-mm-thick asbestos. Hence, this type of device is referred to as an immobilized-alkali fuel cell. The product water is removed from the cell by a hydrogen loop as water vapour. If an alkaline fuel cell with a mobile electrolyte had been used, then the electrolyte would have been diluted by the water produced in the cell. Thus, an

Table 1
Electrode compositions

	Element	Composition (wt.%)	Current collector
Anode (hydrogen electrode)	PTFE (powder)	8	Cu net
	Raney Ni	77	
	Copper (Cu_2O)	15	
Cathode (oxygen electrode)	PTFE (powder)	10	Ni-plated Cu net
	Ag	90	
	Ammonium bicarbonate (40 wt.%)		

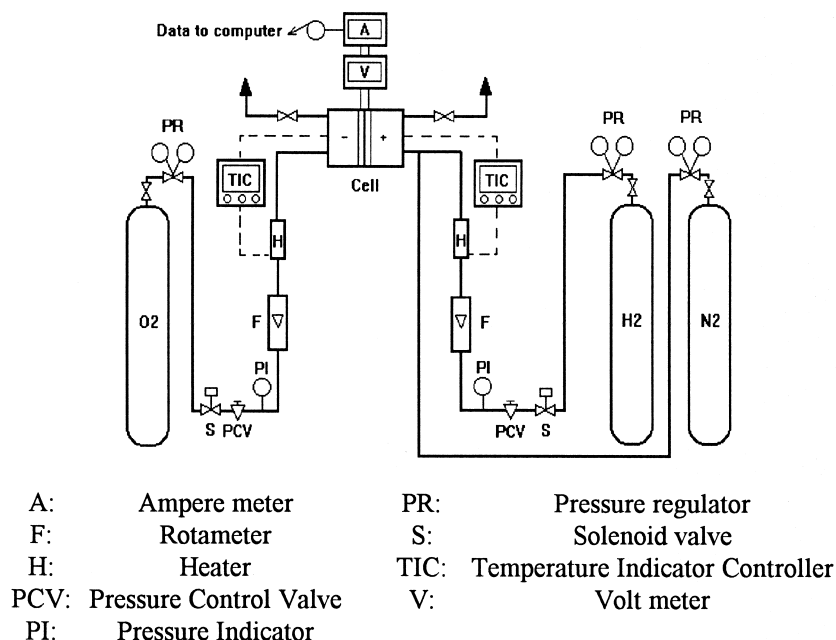


Fig. 1. Schematic of the research cell.

electrolyte regenerator would have been required. Teflon gaskets were employed to provide a reactant seal and to maintain the structural integrity of the cell. Oxygen and hydrogen of high purity (99.999%, Roham Gas, Iran) were employed as the reacting gases. Nitrogen was used as an inert carrier gas.

Two temperature controllers (Shinko, Model ECD-110-R/E, 0–400°C, Japan) were incorporated to maintain the temperature of the system at a constant value. The reacting gases were heated by two electrical heaters. The unreacted gases and gaseous products were flushed out of the fuel cell. Two solenoid valves (Valve, Iran) were employed in the system for to reactant gas supply line. Both gas flows into the cell were measured by glass-tube rotameters (D 47228 Duisburg, Type: RA 60, Germany) which were calibrated for oxygen and hydrogen at the standard state. Two pressure-control valves (Bonesi Pneumatic, Push Lock, Italy) and two pressure regulators (Harris, USA) were used to adjust the inlet pressure of the reactant gases. Two pressure gauges (made in Romania) were filled in both the anolyte and the catholyte sections for indicating the reactant gas concentrations. This assembly was interfaced with a personal computer, through in-house hardware and software, so that the current and the voltage behaviour of the cell was monitored on a computer screen.

3. Results and discussion

3.1. Physical characterization

The structure of a gas-diffusion electrode is highly complex. Major physical properties include: (i) porosity;

(ii) pore-size distribution; (iii) surface area; (iv) permeability; (v) microstructure, (vi) grain size. Usually, an attempt is made to correlate the electrochemical performance of the porous electrodes with one or more of these physical characteristics. Such correlation would assist the construction of a high-performance, low-cost, porous electrode. From the results presented in Table 2, it is obvious that electrodes consist of two types of structures, namely: a primary (i.e., macro) structure which provides the skeleton of the electrode and determines its mechanical strength, and a secondary (i.e., micro) structure which ensures gas transport. Table 2 also shows typical results for the pore volume and the specific surface area for both electrodes made in this project. The surface area of the anode and the cathode is 43 and 14 m²/g, respectively. On the other hand, the corresponding pore volumes are 0.0744 and 0.0255 cm³/g respectively. These quantities are in reasonable agreement with those reported by Al-Saleh et al. [9]. In other words, these researchers determined that the specific surface area for their anode electrode was 20 m²/g and its porosity was 0.049 cm³/g. They also found a BET area of 37 m²/g and a porosity of 0.07 cm³/g for their cathode electrode.

Scanning electron micrographs of the anode and the cathode are given in Fig. 2a and b, respectively. These micrographs confirm the differences in surface area and pore volume between Ni/PTFE and Ag/PTFE electrodes. It is to be noted that all data obtained in this work exhibit good reproducibility.

3.2. Electrochemical evaluation

Tafel plots for hydrogen and for oxygen electrodes are given in Figs. 3 and 4, respectively. These plots are used to

Table 2
Physical characterization of electrodes

Electrode	Pore volume (cm ³ /g)	Surface area (BET) (m ² /g)	Ave. pore diameter (μm)	Pore-size distribution (%)				Ave. grain width (μm)	Grain-size distribution (%)			
				0–1 μm	1–2 μm	2–3 μm	> 3 μm		0–1 μm	1–2 μm	> 2 μm	
Anode	0.0744	43	0.8356	71	20	7	2	0.4889	91	6	3	
Cathode	0.0205	14	8.318	72	20	6	2	19.69	88	7	3	2

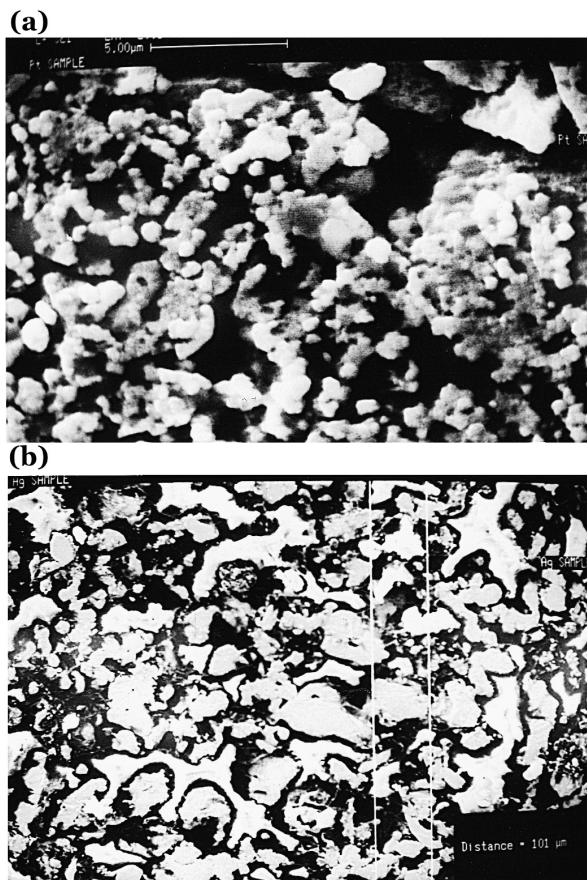


Fig. 2. Electron micrographs of anode and cathode electrodes.

determine kinetic parameters such as the exchange current density (i_0) and charge-transfer coefficient (α) for electrodes at standard temperature and pressure and an alkaline electrolyte concentration of 30 wt.%. The current density/potential relationship depends on three parameters, which include i_0 , and E^0 (i.e., the standard potential). In kinetic studies, the measurement of only two of these is considered, normally α and i_0 (or equivalent quantities). Clearly, the value of α will affect significantly the form of the polarization curve. For this research, the exchange current density of the anode was found to be 1×10^{-6}

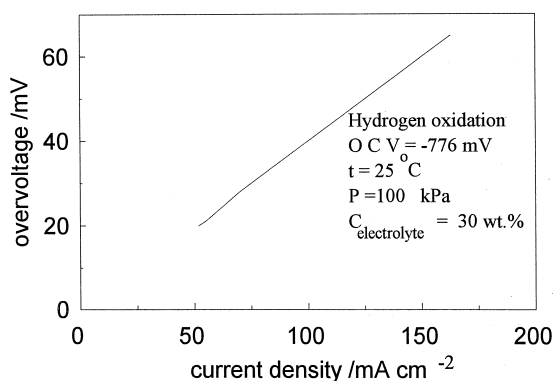


Fig. 3. Tafel plots for hydrogen oxidation reaction at 25°C.

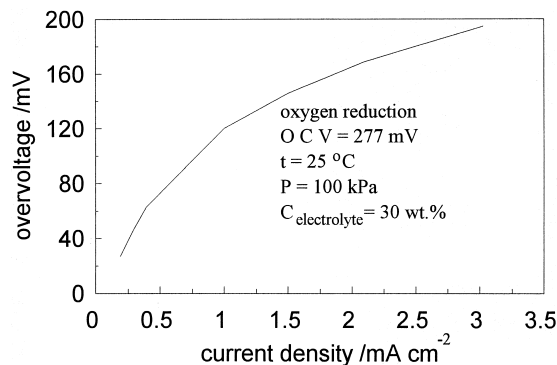


Fig. 4. Tafel plots for reduction reaction at 25°C.

A/cm^2 , and its charge-transfer coefficient was 0.3. For the cathode, these values are $4.3 \times 10^{-9} \text{ A/cm}^2$ and 0.22; respectively. i_0 is a very useful parameter for the description of the electrode reaction kinetics. In other words, it is related to the reaction rate constant. A large value of this quantity represents a high degree of simultaneous redox reaction and is also indicative of inherently fast reactions. High values obtained for exchange current densities in this study raise the expectations for good performance of electrodes.

The performance of an AFC electrode deteriorates with the passage of time. For a commercial alkaline fuel cell system, the long-lived criteria are presented. In this research, electrode deactivation was studied by potentiostatic transient tests for both the anode and the cathode. Through this method, the potential of the test electrode is controlled externally and the time variation of the current density that results from a step-like change in potential is studied. The current decreases with increasing time since the concentration of reactants (H_2 or O_2) or working ions (OH^-) decay due to being consumed. Hence, mass-transfer limitations are imposed upon the system because of the reduction in both the surface area and the pore volume of the electrodes. These results are demonstrated in Figs. 5 and 6. Clearly, cathode deactivation is faster than the anode. The

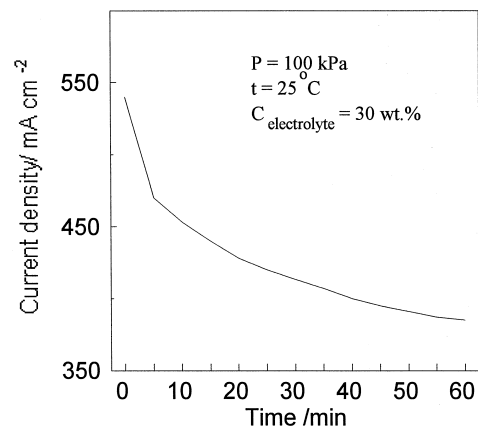


Fig. 5. Potentiostatic transient test at 25°C and 100 kPa for hydrogen oxidation reaction in 30 wt.% KOH solution.

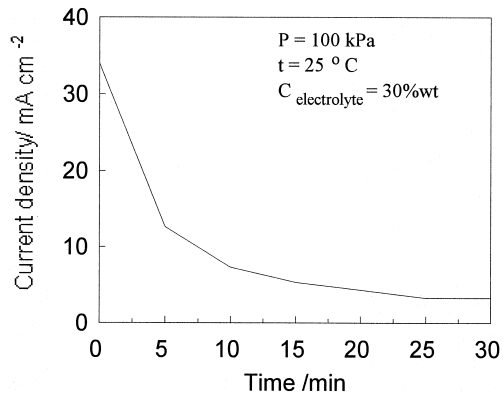


Fig. 6. Potentiostatic transient test at 25°C and 100 kPa, for oxygen reduction reaction in 30 wt.% KOH solution.

difference lies in the fact that the surface area and porosity of the anode are both greater than those of the cathode.

3.3. Fuel cell experiments

The polarization curves for a monocell using H_2 – O_2 at 25°C, and 100 and 200 kPa pressure is given in Fig. 7. Two key parameters obtained from such behaviour are the limiting current (i.e., I_{lim}) which indicates mass-transfer limitations in the system and the open-circuit voltage (V_{oc}) which represents the resistance towards passage of electricity between the anode and the cathode. The limiting current and the open-circuit voltage are 1.8 A and 0.976 V, respectively. In this situation, the efficiency of the fuel cell (η_{fc}) is 66%. Note that the efficiency of any fuel cell is the ratio between the electrical power output and the fuel input, both of which must be in the same units (e.g., watts) [2]. Furthermore, at an operating temperature of 25°C and a reactant pressure of about 200 kPa, the fuel cell can be loaded with a limiting current of 2.2 A and the open-circuit voltage of 1.093 V, thus resulting in a fuel cell efficiency of 74%. It is evident that a pressure increase will enhance the cell performance due to an increase in both I_{lim} and V_{oc} of the system.

The effect of temperature at a constant pressure of 100 kPa on the polarization behaviour of the system is demon-

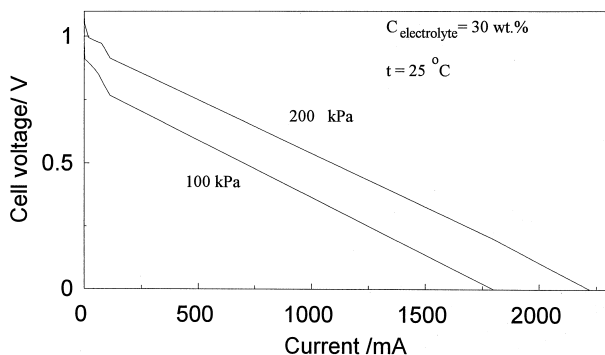


Fig. 7. Pressure influence on fuel cell polarization curve.

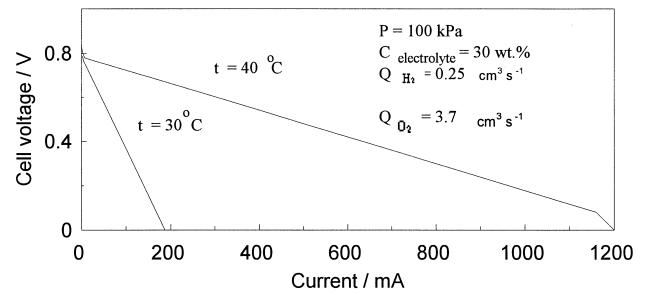


Fig. 8. Temperature influence on fuel cell polarization curve.

strated in Fig. 8. It is seen that when the temperature is raised, an improved cell performance is obtained. Furthermore, a quick comparison between the effect of pressure and temperature on the cell performance points to the fact that a rise in temperature affects cell efficiency in a more pronounced manner. This is due to a higher increase in the kinetics compared with mass-transfer parameters that arise from these changes.

4. Conclusions

A new electrode preparation method has been developed. The structural parameters strongly influence the performance characteristics of PTFE-bonded, porous gas-diffusion electrodes. BET analysis, porosimetry, SEM and electrochemical evaluation (including Tafel and potentiostatic tests) reveal that the electrodes are composed of a primary (macro) and a secondary (micro) electrode structure.

A fuel cell test module has been designed and constructed to determine the performance of an alkaline fuel cell. The fuel cell is a single, hydrogen–oxygen, immobilized-alkaline electrolyte type. Its performance results from a combined action of diverse effects that depend upon structural and operational parameters. In this type of system, as the temperature increases, the performance also rises. In fact, the temperature dependence of the exchange current densities at the oxygen and hydrogen electrodes are of the Arrhenius type, hence the observed voltage increase (with temperature) may be explained by this phenomenon. The influence of operating gas pressure on the performance of the fuel cell is also investigated. It is concluded that the resulting cell voltage increases with rise in pressure.

The performance of the fuel cell has, ultimately, been studied by means of polarization curves. At temperature of 25°C and pressure of 100 kPa, an overall efficiency of 66% is obtained while at pressure of 200 kPa this efficiency increases to 74%. These might be due to mass-transfer versus kinetic interactions taking place in the system.

Acknowledgements

Authors gratefully acknowledge the financial support received from the Renewable Energy Organization of Iran, SUNA, affiliated to the Ministry of Energy of the I.R. of Iran.

References

- [1] K. Joon, J. Power Sources 71 (1998) 12.
- [2] F. Barbir, T. Gomez, Int. J. Hydrogen Energy 22 (1997) 1027.
- [3] M.T. Ergul, L. Turker, I. Erogul, Int. J. Hydrogen Energy 22 (1997) 1039.
- [4] P. Staiti, S. Hocevar, N. Giordano, Int. J. Hydrogen Energy 22 (1997) 809.
- [5] A. Khalidi, B. Lafage, P. Taxil, G. Gave, M.J. Clifton, P. Cezac, Int. J. Hydrogen Energy 21 (1996) 25.
- [6] E. Guelzow, J. Power Sources 61 (1996) 99.
- [7] D. Staschewski, Int. J. Hydrogen Energy 17 (1992) 643.
- [8] A.O. McDougall, in: Fuel Cells, Butler and Tanner, London, 1976, p. 54.
- [9] M.A. Al-Saleh, S. Gultekin, A.S. Al-Zakri, H. Celiker, J. Appl. Electrochem. 24 (1994) 575.
- [10] M.A. Al-Saleh, S. Gultekin, A.S. Al-Zakri, A.A.A. Khan, Int. J. Hydrogen Energy 21 (1996) 657.