



Composite Electrode for Unitized Regenerative Proton Exchange Membrane Fuel Cell with Improved Cycle Life

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To improve the cycle life of unitized regenerative fuel cells (URFCs), an electrode with a composite structure has been developed. The cycle life and polarization curves for both fuel cell and electrolysis modes of URFC operation were investigated. The cycle life of URFCs was improved considerably and the performance was fairly constant during 25 cycles, which illustrates that the composite electrode is effective in sustaining the cyclic performance of URFCs. It shows the URFCs with such an electrode structure are promising for practical applications.

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A regenerative fuel cell (RFC) is a battery-like hydrogen/oxygen system,¹ which offers the possibility of splitting water by a proton exchange membrane water electrolyzer (PEMWE), storing the hydrogen and oxygen gas, and then generating electricity by the proton exchange membrane fuel cell (PEMFC). It has the advantage of long-term energy storage and theoretically higher energy densities compared to secondary batteries (*i.e.*, lead acid, Ni/Cd, Ni/MH, and Li-ion²). To date, such systems have been developed for space and military applications.¹ However, RFCs are usually complicated and expensive because RFCs use two separate electrochemical devices: fuel cell and water electrolyzer. This problem could be overcome by developing a unitized regenerative fuel cell (URFC). URFC is an electrochemical cell working both as a water electrolyzer and a fuel cell.³⁻¹⁰ In these systems, one electrode is used solely for the oxygen electrode (oxygen evolution in the electrolysis mode, oxygen reduction in the fuel cell mode), whereas the other electrode operates as the correspondent hydrogen electrode (hydrogen evolution in the electrolysis mode, hydrogen oxidation in the fuel cell mode). A simpler and more compact RFC system can be constructed by using URFC. The distinct superiorities of the URFC system are lower cost, weight, and volume than a conventional RFC.

URFCs are promising energy storage systems for uninterrupted power supplies, solar-powered aircraft, satellites, and microspacecraft. Other applications of a URFC may include an on-site energy storage system for load leveling of utility grids or renewable energy such as photovoltaic and wind energy.

The key issues in URFC development are to improve the cycle life and reduce the cost, *i.e.*, the catalyst loadings, thus it is necessary to develop the optimized oxygen electrode structure and composition. We previously reported the thin-film electrocatalyst layers (TFELs) used for URFCs with a catalyst loading as low as 0.4 mg/cm² and a satisfactory performance.⁶ Recently, TFELs with various polytetrafluoroethylene (PTFE) and Nafion contents for URFCs were prepared and evaluated,¹⁰ the catalyst loadings being reduced to 2-4 mg/cm² without degrading the URFC performance. It was demonstrated that TFELs are effective and feasible for URFC development. However, the data of cycle life was not provided.¹⁰ In our previous study,⁶ the URFC showed only an initial stability during a short test of four to six cycles, so further efforts are necessary to develop a better electrode structure to improve cycle life.

In this study, the electrode with a composite structure for the URFC was developed to improve cycle life and the catalyst loadings were kept at a moderate level by modifying the TFELs electrode preparation method. The cycle life and the voltage *vs.* current density (*I-V*) curves for both fuel cell and electrolysis modes of URFC operation were evaluated. Preliminary results showed that cycle stability of URFCs is improved substantially with the composite electrode.

Experimental

Preparation of electrocatalyst.—Platinum black was used as a bifunctional hydrogen catalyst, while platinum black and iridium oxide were used as a bifunctional oxygen catalyst. Platinum black was made from H₂PtCl₆ by HCHO reduction.¹¹ Iridium oxide was made by proprietary modification of an Adams-type fusion of the iridium salt in a nitrate flux.¹²

Preparation of composite electrode.—The composite electrode includes a TFEL and a catalyzed gas diffusion layer (CGDL) that was prepared separately. A schematic diagram of the cross section of the composite electrode is shown in Fig. 1. A transfer printing technique^{13,14} was used to make the TFEL with a thickness of about 5 μm. Glycerol was used to produce pores in TFEL. 50 wt % Pt and 50 wt % IrO₂ were used as the bifunctional electrocatalyst for the oxygen electrode of the TFELs, the loading of each catalyst being 0.2 mg/cm². Pt was used as the bifunctional electrocatalyst for the hydrogen electrode of the TFELs with a loading of 0.4 mg/cm². Details of the preparation procedure were described previously.⁶ The TFELs and membrane assembly were made by compressing tightly the TFELs and proton exchange membrane (Nafion 115, DuPont Corp.) together at high temperature (180°C).

For the CGDL, a carbon paper (SGL, Germany) treated by PTFE was used as substrate, which contained about 40 wt % PTFE. Then a homogeneous suspension of 40 wt % PTFE and 60 wt % carbon (Vulcan XC-72R), referred to as carbon ink, was brushed on the carbon paper followed by calcination at 340°C to form a gas diffusion layer. An electrocatalyst ink, which was prepared by homogeneously dispersing the 60 wt % electrocatalyst (Pt or Pt and IrO₂) and 40 wt % PTFE in isopropanol, was applied on the gas diffusion layer followed by sintering at 340°C. Finally, 0.3 mg/cm² Nafion solution (DuPont Corp.) was sprayed on the surface of the electrocatalyst layer and dried at room temperature to form the CGDL. Both the hydrogen and oxygen side of the CGDLs were prepared in the same manner. For the oxygen side, 2 mg/cm² Pt and 1.5 mg/cm² IrO₂ were applied, while for the hydrogen side, Pt was used as electrocatalyst with a loading of 0.4 mg/cm². The CGDLs of oxygen and hydrogen were placed on both sides of the TFELs and membrane assembly and hot-pressed at 150°C to form the electrode with composite structure.

Evaluation of URFC cycle performance and electrochemical polarization.—Evaluation of URFC cycle performance was conducted in a single cell with an effective electrode area of 5 cm² (geometric). During fuel cell operation, humidification of the reactant hydrogen gas was accomplished by bubbling the gases through a humidifier. During water electrolysis operation, purified water was supplied to the positive electrode of the single cell by a pump. Before and after the cycle test, the electrochemical polarization curves (*I-V* curves) were taken for both fuel cell and electrolysis modes at different temperatures. During the cycle test, data for fuel

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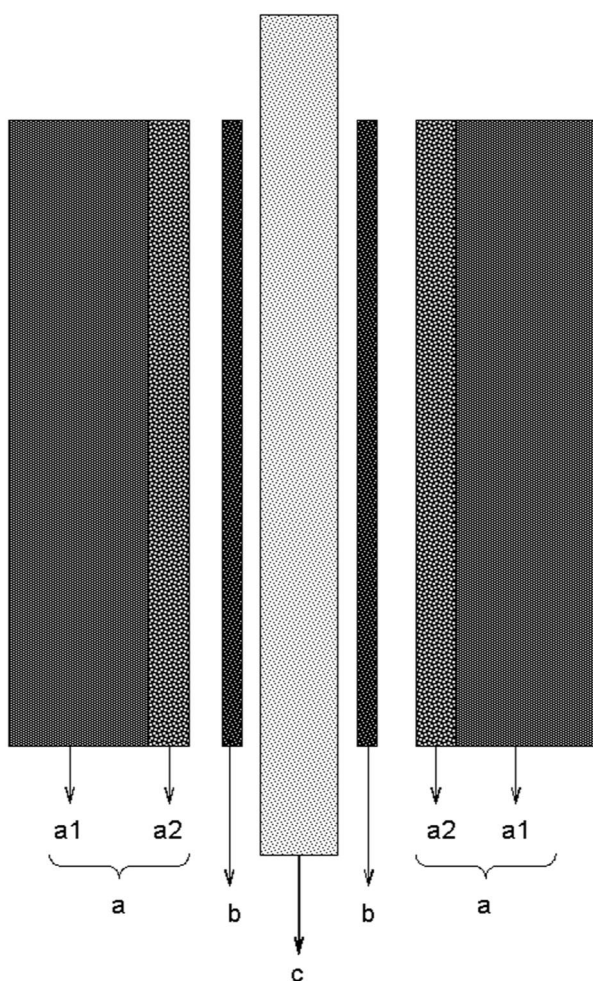


Figure 1. Schematic illustration of the cross section of the composite electrode: (a) CGDL consisting of (a1) gas diffusion layer and (a2) electrocatalyst layer; (b) TFEL; (c) proton exchange membrane.

cell operation mode were collected first, and then the cell was run at electrolysis mode. After data collection in that mode, the cell was operated as a fuel cell again. The cycle of fuel cell-electrolysis was then repeated continuously. Generally, the period for fuel cell mode was 2 h and for electrolysis mode, it was 1 h.

To verify the cyclic performance of URFC and to meet the requirements of the possible rigorous conditions in practical applications, the temperature was strictly controlled. During fuel cell operation, the single cell was operated at 40°C on H₂/O₂ with anode/cathode pressures of 0.4/0.4 MPa. The temperature of hydrogen humidification was 50°C. During water electrolysis operation, the cell and water reservoir were kept at ambient temperature (about 20°C) with atmospheric pressure. During fuel cell mode, the *I-V* polarization curves were collected at the beginning and the end, and the fuel cell was run at 400 mA/cm² during the interval. For electrolysis mode, the current density of electrolysis was fixed as 320 mA/cm² during the overall running period.

Results and Discussion

Typical URFC terminal voltage for electrolysis and fuel cell during a cycle are shown in Fig. 2, which was measured in the 18th cycle. The cyclic performance of URFC is illustrated in Fig. 3. Figure 4 shows the electrolysis voltage vs. current density curves of URFC at different temperatures before and after cycle test. The change for the fuel cell performance during different cycles is demonstrated by the *I-V* curves in Fig. 5.

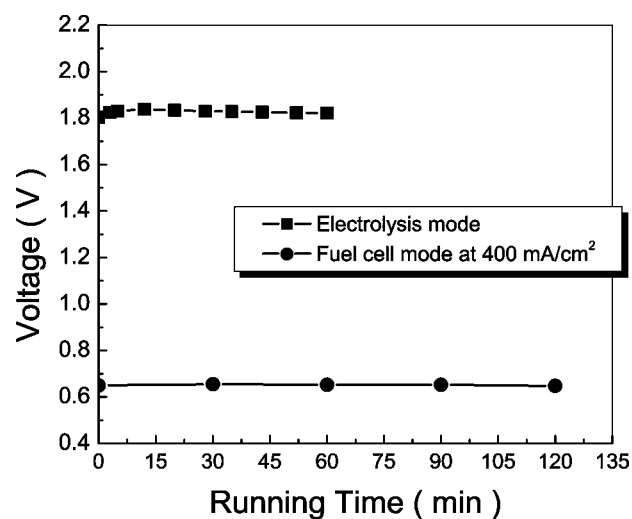


Figure 2. Electrolysis and fuel cell behavior of the URFC during 18th cycle; Nafion 115 membrane.

It can be seen from Fig. 2 that the URFC has a lower voltage of electrolysis even in such a low temperature and a high current density of electrolysis. The average voltage of electrolysis is 1.822 V. The terminal voltages of electrolysis during 25 cycles are shown in Fig. 3. These results show that the URFC has a good performance for electrolysis mode. The fuel cell performance at 40°C is important in the context of URFC engineering. Higher temperatures are typically employed in URFC because of the performance advantages, but the significant simplifications in component and system design would be possible if the temperature requirement could be relaxed. Figure 3 also illustrates the performances of the fuel cell operated at 40°C during the cyclic test. The average terminal voltage of the fuel cell was 0.723 V at 300 mA/cm² and 0.645 V at 400 mA/cm² and it can reach 0.738 V at 300 mA/cm² and 0.665 V at 400 mA/cm², which is promising for practical applications.

It can be seen from Fig. 2 that the cell voltages were stable during the longer test time on both modes of electrolysis and fuel cell in one cycle test. In Fig. 3, the URFC performance was fairly constant for both running modes during 25 cycles. These results show that the cyclic performance of URFC was improved considerably over the one reported previously.⁶ The stable cyclic perfor-

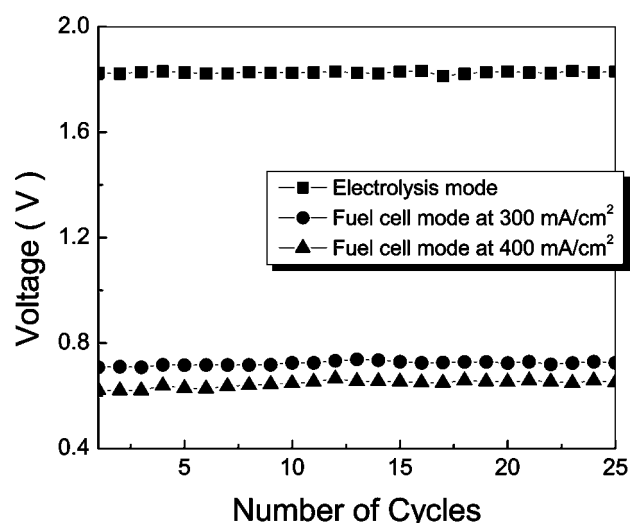


Figure 3. Performances of fuel cell/electrolysis of URFC as a function of number of cycles; Nafion 115 membrane.

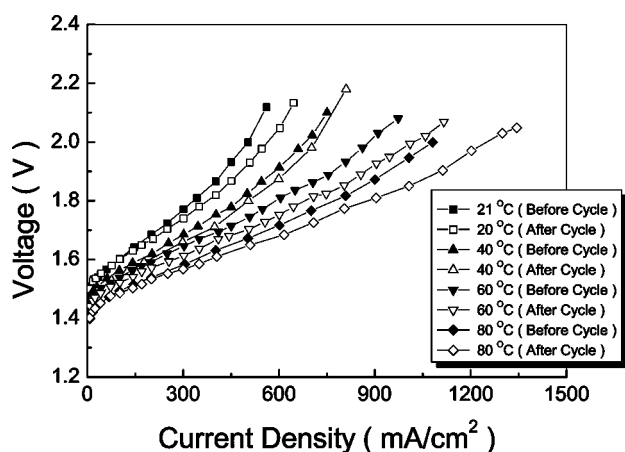


Figure 4. Voltage of electrolysis vs. current density curves of URFC at different temperatures before and after cycle test; Nafion 115 membrane.

mance of URFC is related to the suitable structure of electrode. There are different requirements operated at different modes. The requirements for electrolysis application are as follows: the electrode must be corrosion resistant, the electrocatalytic activity for oxygen evolution reaction must be high,^{4,9} and the electrode structure must be sufficiently porous to allow fluid transport (reactant (H_2O) and products (O_2, H_2)). At the same time, the mechanical stability and electronic conductivity must be preserved. The ideal electrode structure for PEMFC must satisfy three criteria to contribute to the electrochemical reaction in a fuel cell. The criteria are proton access, gas access, and electronic path continuity.¹⁵⁻²⁰ For gas access, PTFE is needed because it can facilitate gas diffusion by providing hydrophobicity to the pore to prevent it from being clogged with water.

In the composite electrode, the TFELs and the CGDLs are assuming different functions for the electrolysis and fuel cell operation, respectively. The main role of the TFELs is to work at the electrolysis mode. The TFELs were prepared to be fully hydrophilic without PTFE, because it has been shown that the water electrolysis performance scarcely depended on the PTFE content in the TFELs.¹⁰ Furthermore, the hydrophilic TFEL provides a good adhesion between it and the membrane,^{6,13} which is extremely important for the cycle life of URFC because the electrodes must sustain high mechanical tension during gas evolution. Much attention has been devoted to strengthen the bonding of the electrode onto the membrane.²¹⁻²³ The TEFLs and membrane assembly met the somewhat severe requirements in the present study. The TFELs in this

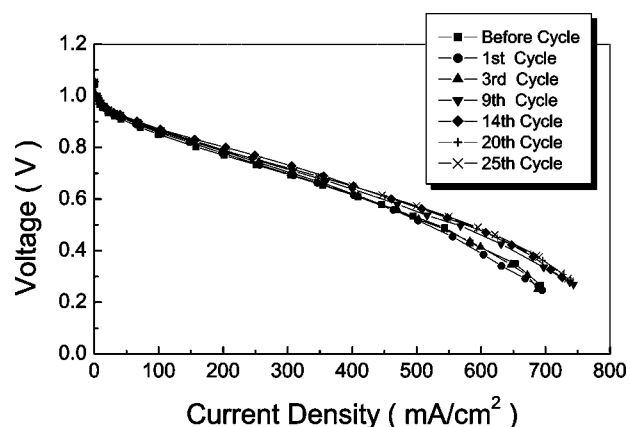


Figure 5. Performances of fuel cell of URFC during different cycles; Nafion 115 membrane.

work provide a sufficient amount of pores for reactant and product transport, so a satisfactory performance could be achieved with electrocatalyst loadings as low as 0.4 mg/cm^2 .

According to our previous study,⁶ it has been shown that electrolysis performance was fairly constant but the fuel cell performance decreased in the cycle test. The main reason was that the electrodes were flooded, especially on the cathode side, which severely blocked gas access to the three-phase active area. Compared to electrolysis mode, opposite water management is required for fuel cell operation, *i.e.*, appropriate hydrophobicity is required during fuel cell mode. Therefore, the CGDLs, which were fabricated by the conventional preparation technology of hydrophobic electrodes for PEMFC and with the needed functions used in URFC, were devised to take a major role in the function as fuel cell. In the CGDL, carbon paper and carbon powder treated by PTFE were utilized as gas diffusion layer. The electrocatalyst layer was treated by PTFE as well. Thus, both of them are hydrophobic to some extent during the longer term cycle test. It can provide effective gas pathways for URFC operated at fuel cell mode, particularly for oxygen reduction reaction.

The stable performance of URFC is related to the roles of TFELs during fuel cell operation and the ones of CGDLs during electrolysis operation as well. During the fuel cell reaction, hydrogen ion could reach favorably the electrocatalyst layers of CGDL because the TFEL was very thin and there was enough Nafion to conduct H^+ , so it was not detrimental to the fuel cell performance. Despite the hydrophilicity of the TFEL, the permeability of oxygen through the TFEL is sufficient such that a $5 \mu\text{m}$ diffusion pathway through the ionomer to the catalyst particles will not introduce significant oxygen transport losses,²⁴ so TFEL could be considered as the extension of CGDL in fuel cell operation.

Meanwhile, in the electrolysis mode, water and O_2, H_2 products could diffuse effectively because there were sufficient pores in both the gas diffusion layer and the electrocatalyst layer of CGDL, so the performance of electrolysis would not be affected by the presence of CGDL.

The porous carbon in the gas diffusion layer of CGDL is a good current conductor and fluid distributor in PEMFC, but it is not stable as an anode for oxygen evolution.^{3,25} From Fig. 4 and 5, it is indicated that the electrolysis and fuel cell performances after cycle test are all superior to the ones before cycle test. It is known that carbon is destroyed mainly during the oxygen evolution process, and the corrosion of carbon subsequently degrades the fuel cell performance. So it shows that carbon in the composite electrode may well be protected. A possible explanation is that even though the intermediates such as $OH\cdot$ radical,²⁶⁻²⁸ atomic oxygen,^{26,27} or $HO_2\cdot$ radical²⁸ produced in TFEL during the electrolysis cannot combine entirely to O_2 , and even desorbed from the active surface sites of the electrocatalysts, they could form oxygen molecule sufficiently in the bulk electrocatalyst layer of CGDL on the unsupported, stable, and highly active electrocatalysts of Pt and IrO_2 . Thus, the electrocatalyst layer can prevent the intermediates with strong oxidative reactivity from reaching the gas diffusion layer and attacking the carbon atoms, causing carbon corrosion. Consequently, the suitable pore structure, electron conductivity, and hydrophobicity in CGDL were protected and the performance of electrolysis (also the fuel cell) could be retained during the cyclic test. As for the performance improvement of URFC after cycle test, a possible reason may be that Nafion resin attained better hydration after several cycles, so the conduction of H^+ in electrocatalyst layers was improved. From the above discussion, it can be seen that the composite electrode is a promising way to prepare electrodes for practical application of URFC.

Even though the composite electrode described here is feasible for improving cycle life for URFC, further work is still necessary to optimize the two-part construction of the electrode, CGDLs and TFELs, to obtain better performances.

Conclusion

A composite electrode was prepared and the performance of the URFC using such electrode was investigated. The cycle life of URFC was improved considerably with this novel electrode structure, which kept the performance fairly constant for both modes of electrolysis and fuel cell over 25 cycles. It implies that the composite electrode is promising for the practical application of URFC.

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References

1. R. Baldwin, M. Pham, A. Leonida, J. Mcelroy, and T. Nalette, *J. Power Sources*, **29**, 399 (1990).
2. K. Bolwin, *J. Power Sources*, **40**, 307 (1992).
3. L. L. Swette, A. B. LaConti, and S. A. McCatty, *J. Power Sources*, **47**, 343 (1994).
4. T. Ioroi, N. Kitazawa, K. Yasuda, Y. Yamamoto, and H. Takenaka, *J. Electrochem. Soc.*, **147**, 2018 (2000).
5. K. Ledjeff, F. Mählendorf, V. Peinecke, and A. Heinzl, *Electrochim. Acta*, **40**, 315 (1995).
6. Z. Shao, B. Yi, and M. Han, *J. Power Sources*, **79**, 82 (1999).
7. H. P. Dhar, *J. Appl. Electrochem.*, **23**, 32 (1993).
8. F. Mitlitsk, B. Myers, and A. H. Weisberg, *Energy Fuels*, **12**, 56 (1998).
9. G. Chen, S. R. Bare, and T. E. Mallouk, *J. Electrochem. Soc.*, **149**, A1092 (2002).
10. T. Ioroi, K. Yasuda, Z. Siroma, N. Fujiwara, and Y. Miyazaki, *J. Power Sources*, **112**, 583 (2002).
11. J. Giner, J. M. Parry, and S. M. Smith, *Fuel Cell System-II*, 151 (1969).
12. R. Adams and R. L. Shriner, *J. Am. Chem. Soc.*, **45**, 2171 (1923).
13. M. S. Wilson and S. Gottesfeld, *J. Appl. Electrochem.*, **22**, 1 (1992).
14. M. S. Wilson and S. Gottesfeld, *J. Electrochem. Soc.*, **139**, L28 (1992).
15. M. S. Wilson, J. A. Valerio, and S. Gottesfeld, *Electrochim. Acta*, **40**, 355 (1995).
16. S. Mukerjee, S. Srinivasan, and A. J. Appleby, *Electrochim. Acta*, **38**, 1661 (1993).
17. H.-F. Oetjen, V. M. Schmidt, U. Stimming, and F. Trila, *J. Electrochem. Soc.*, **143**, 3838 (1996).
18. T. R. Ralph, G. A. Hards, J. E. Keating, S. A. Campbell, D. P. Wilkinson, M. Daris, J. St-Pierre, and M. C. Johnson, *J. Electrochem. Soc.*, **144**, 3845 (1997).
19. J. S. Wainright, J.-T. Wang, R. F. Savinell, and M. Litt, *J. Electrochem. Soc.*, **142**, L121 (1995).
20. J.-T. Wang, R. F. Savinell, J. Wainright, M. Litt, and H. Yu, *Electrochim. Acta*, **41**, 143 (1996).
21. A. Katayama-Akamata, H. Nakajima, K. Fujikawa, and H. Kita, *Electrochim. Acta*, **28**, 777 (1983).
22. H. Kita, F. Fujikawa, and H. Nakajima, *Electrochim. Acta*, **29**, 1721 (1984).
23. H. Nakajima, Y. Takakuwa, H. Kikuchi, F. Fujikawa, and H. Kita, *Electrochim. Acta*, **32**, 791 (1987).
24. S. Gottesfeld, I. Raistrick, and S. Srinivasan, *J. Electrochem. Soc.*, **134**, 1455 (1987).
25. A. Hamnett, P. S. Stevens, and R. D. Wingate, *J. Appl. Electrochem.*, **21**, 982 (1991).
26. K. Darowicki and J. Orlikowski, *J. Electrochem. Soc.*, **146**, 663 (1999).
27. G. Chen, X. Chen, and P. L. Yue, *J. Phys. Chem. B*, **106**, 4364 (2002).
28. T. R. Beck and R. W. Moulton, *J. Electrochem. Soc.*, **103**, 247 (1956).