Alkaline Fuel Cell with Intrinsic Energy Storage

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A new high peak power density alkaline fuel cell (FC) was fabricated using a metal hydriding (MH) alloy as the anode electrocatalyst and manganese dioxide as the cathode electrocatalyst. The high-loading MH and MnO2 electrocatalysts not only gave a satisfactory steady-state power output, but also deliver additional power stored in the charged MH and MnO2 electrodes when the overall cell voltage fell. Moreover, the MH/MnO2 FC can still deliver a certain amount of energy even after the hydrogen and oxygen are shut off. The discharged MH and MnO2 electrodes are recharged by hydrogen and oxygen in the FC when the cell voltage returns to normal levels. This MH/MnO2 alkaline FC performs the same functions as those of a more complex fuel cell/battery hybrid system with lower weight, volume, and cost.

AFCs show promise as environmentally friendly electrochemical power sources for distributed cogeneration for building, and transportation applications. As with other FCs, the continuous power output of AFCs is satisfactory, however, their response to instantaneous power load requirements may often be insufficient. To meet such peak power requirements, the AFC must be hybridized with a second battery, a supercapacitor, or both. Normally, AFC/battery/supercapacitor systems use separate components connected by an electrical control system. This results in increased complexity, weight, volume, and cost. One solution is to incorporate a battery element into the FC, e.g., using energy storage materials as electrocatalysts in the electrodes. Such electrode materials should have a high energy storage capacity and have good electrocatalytic activity for anodic hydrogen oxidation and cathodic oxygen reduction.

Metal hydride (MH) alloys and manganese dioxide are excellent electrocatalysts for hydrogen oxidation and oxygen reduction, respectively. In fact, the generic electrolyte-resistant AB2 alloys, whose parent material is LnNi5, have been successfully used as anode catalyst in AFCs, 1,2 and MnO2 has been evaluated as an electrocatalyst for oxygen reduction in alkaline solution. 3 Hence, selected MH materials and MnO2 may be used as electrocatalysts in AFCs. On the other hand, hydrogen or proton from water can reversibly be inserted into or be extracted from MH compounds and MnO2 over the appropriate potential ranges in alkaline solution. Hence, MH anodes and MnO2 cathodes in alkaline solution may be used as a rechargeable alkaline cell. 5,6 Recent results show that such cells has several advantages, particularly long cycle life under the correct conditions, no memory effect, high capacity, nontoxicity, low self-discharge rate, high performance, and high cost-effectiveness. 8 Therefore, an alkaline FC with high-loading MH compound as the anode electrocatalyst and high-loading MnO2 as the cathode electrocatalyst may be given the same functions as those of a complex FC/battery hybrid system, with a consequent reduction in system weight, volume, and cost. Compared to the proton exchange membrane fuel cell (PEMFC) and the direct methanol fuel cell (DMFC), an MH/MnO2 AFC has a potentially lower cost due to less costly electrolyte and non-platinum-metal electrocatalysts. Another advantage of the MH/MnO2 AFC is that it can deliver a certain energy even after the hydrogen and oxygen supplies are turned off.

This paper describes AFCs with high loading MH anodes and high loading of MnO2 cathodes for the first time, and reports their performance during continuous and instantaneous loads, even with interrupted fuel and oxidant supply.

Experimental

Preparation of electrodes and cells.—The MH and MnO2 electrodes consisted of a hydrophobic gas diffusion layer on the gas side and an active electrocatalyst layer facing the electrolyte. The gas diffusion layer was identical for both electrodes, and was prepared by rolling wet-proofed (35 wt % poly(tetrafluoroethylene, PTFE) acetylene black onto nickel mesh, followed by sintering in an oven at 300°C for 15 min. The MH electrocatalyst layer used the lanthanide mischmetal-based (Lm) alloy LmNi4.1Co0.4Mn0.4Al0.3 (200 mesh, Japan Metal & Chemicals Co. Ltd), which was first mixed with nickel powder and wet-proofed (60 wt % PTFE) acetylene black in the mass ratio 60:30:4:6 (MH:Ni:C:PTFE). The mixture was mechanically milled for either 10 or 30 min in a SPEX CertiPrep model 8000M mixer/mill. Pure ethanol was added to the milled mixture, which was then rolled onto the gas diffusion layer to form into thin-film type MH anode. Electrodes with three different MH loadings (150, 100, 60 mg/cm2) were prepared by changing the thickness of the active layer. As with Raney nickel electrocatalysts, LmNi4.1Co0.4Mn0.4Al0.3 requires an initial activation i.e., electrochemical charge, a process to fracture or remove the oxide film on the alloy surface. To reduce or eliminate activation requirements, LmNi4.1Co0.4Mn0.4Al0.3 was also mixed with 0.5 wt % of platinum electrocatalyst in the form of 10 wt % Pt on Vulcan XC72 carbon black (E-TEK, Inc., (Natick, MA). For the cathode, MnO2 powders (Alfa Johnson Matthey) were first mixed with graphite in the mass ratio of 1:1, and then mechanical milled for either 5 min or 50 h. A 60 wt % PTFE dispersion was then added to the milled mixture to give a mass ratio 45:45:10 (MnO2:graphite:PTFE). As for the anode, ethanol was added to the milled mixture, which was then rolled onto the gas diffusion layer to form thin-film cathodes with different MnO2 loadings (150, 100, and 60 mg/cm2).

Figure 1 shows the structure of the MH/MnO2 test cells. The geometrical surface areas of MH and MnO2 electrodes in contact with 6 M KOH electrolyte was 1 cm2, and the distance between the anode and cathode was 1.0 cm. An Hg/HgO reference electrode was inserted through a small hole in the center plate. The electrolyte was replaced with fresh electrolyte from time to time via a hole in the cell. Namely atmospheric-pressure hydrogen and oxygen were supplied behind the electrodes at a stoichiometry of 2.0.

To independently determine the performance of MH and MnO2 electrodes as rechargeable battery electrodes, they were prepared without gas diffusion layers and were each pressed between two nickel-mesh current collectors to form pellets of 2.0 cm2 geometric
area and 1.2 mm thickness. The MH or MnO$_2$ electrodes were placed in the center of a four-compartment glass cell, which had two large area Ni(OH)$_2$ /NiOOH electrodes (Hughes Aircraft Company) on either side, and an Hg/HgO reference electrode in the fourth compartment. The 6 M KOH electrolyte was prepared from reagent grade material and deionized (DI) water.

Electrochemical measurement.—The potential-current density (I-E) parameters of test MH/MnO$_2$ AFCs using hydrogen and oxygen were obtained using cyclic voltammetry (CV) at a scan rate of 1.0 mV/s at room temperature. The electrode potentials were measured vs. the Hg/HgO/6M KOH reference electrode at 25°C. All potentials given below are vs. this electrode.

The MH electrode without the 0.5 wt % Pt addition was first activated by charging the cell with charge current of 150 mA/g until the potential of MnO$_2$ reached +0.4 V. This process was repeated five times with a 1.0 h rest period between charges. The catalyst prepared by mechanically milling MH/graphite mixture for 30 min was easily activated because of its fractured oxide film. The electrocatalysts with added Pt develop a sufficiently low open-circuit potential (OCP) in the presence of hydrogen to allow its absorption by MnO$_2$. The resulting volume change rapidly fractures the oxide film, so such electrocatalysts do not require preactivation.

The battery performance of MH and MnO$_2$ electrodes in 6 M KOH electrolytes was measured by charging MH at a mass current density of 50 mA/g for 6.0 h and charging MnO$_2$ at the same current to +0.4 V, with discharge under the same current conditions to an end-of-discharge potential of −0.6 V for MH electrodes and −0.7 V for MnO$_2$ electrode using an Arbin Corporation (College Station, TX) battery cycler.

Electrochemical impedance spectroscopy (EIS) of the MH/MnO$_2$ FC was measured at OCP, −0.9 and −0.85 V for MH electrodes, and at the OCP, −0.05, −0.1, and −0.15 V for MnO$_2$ electrodes in the frequency range 65 KHz to 1 mHz at 5 mV potentiostatic signal amplitude using a Solartron FRA 1250 frequency response analyzer and a Solartron model 1286 electrochemical interface. Before EIS measurements, the electrodes were left at open circuit for 15 min.

Results and Discussion

Performance of MH/MnO$_2$ FC.—Figure 2 shows the current-potential (I-E) performance of LmNi$_{4.1}$Co$_{0.4}$Mn$_{0.4}$Al$_{0.3}$/MnO$_2$ fuel cells measured by CV at 1.0 mV s$^{-1}$ on H$_2$ and O$_2$ at 25°C. The performance of an AFC with Zetek (Geel, Belgium) electrodes (0.3 mg/cm$^2$ platinum on Vulcan XC-72 at both anode and cathode) is shown for comparison. The performance of MH/MnO$_2$ cells with electrocatalyst loadings of 150 mg/cm$^2$ was similar to that of the Zetek cell.

The addition of 0.5 wt % Pt into MH electrocatalyst decreased the hydrogen oxidation overpotential. When the loading was decreased from 100 mg/cm$^2$ to 60 mg/cm$^2$ (with 0.5 wt% Pt addition), the overpotential was relatively independent of electrocatalyst loading (Fig. 2). The electrocatalytic activity of MnO$_2$ electrodes with loadings in excess of 60 mg/cm$^2$ for oxygen reduction were comparable to that of electrodes with commercial Pt electrocatalyst, and their activity increased with loading.

MH and MnO$_2$ electrodes not only had a high catalytic activity for hydrogen oxidation and oxygen reduction, but also showed effective chemical energy storage. At the OCP or under continuous power output operation, the MH and MnO$_2$ electrodes are charged by hydrogen and oxygen. When the voltage was suddenly stepped from the OCP to a low voltage, a large additional current was supplied from the electrodes. Figure 3 shows the current as a function of time for MH containing 0.5 wt% Pt and MnO$_2$, both at 100 mg/cm$^2$ loading when the cell voltage was stepped from to OCP to 0.4 V. As expected, the dependence of current on time in Fig. 3 shows a typical battery performance under voltage step conditions. The current quickly decreased from an initial value of 180 to 125 mA/cm$^2$, and then slowly decreased to a steady-state current of

![Figure 1. Structure of laboratory MH/MnO$_2$ AFC.](image1.png)

![Figure 2. I-E performance of MH (LmNi$_{4.1}$Co$_{0.4}$Mn$_{0.4}$Al$_{0.3}$) anode-MnO$_2$ cathode AFCs as a function of catalyst loading. The performance of an AFC with commercial Zetek Pt/C electrodes (0.3 mg/cm$^2$ loading) is also shown for comparison. Performance measured by CV at 1.0 mV s$^{-1}$ with H$_2$ and O$_2$ as fuel at 25°C.](image2.png)

![Figure 3. The dependence of current on time of a FC when cell voltage was stepped from open-circuit voltage to 0.4 V. Anode MH with 0.3 wt % Pt as Pt/C, cathode MnO$_2$. Catalyst loading 60 mg/cm$^2$ at both electrodes.](image3.png)
around 100 mA/cm², which is close to the value determined by CV at 1.0 mV/s (Fig. 2) at the same cell voltage. The current in excess of 100 mA/cm² results from energy stored in the MH and MnO₂ electrodes. Therefore, incorporating the MH/MnO₂ battery element into an alkaline FC not only increased the continuous power output of the fuel cell (Fig. 2), but also enhanced its peak power output as is shown in Fig. 3.

Discharge performance of MH/MnO₂ FC with H₂ and O₂ interrupted.—When the H₂ and O₂ supplies are shut off, the cell continues to supply power as an MH/MnO₂ battery. Figure 4 shows the potential behavior of the LmNi₄.₁Co₀.₄Mn₀.₄Al₀.₃ and MnO₂ electrodes as a function of time at a discharge current of 14 mA/cm² under these conditions. H₂ and O₂ were resupplied to electrodes with 100 mg/cm² MH and MnO₂ loadings when the potential of the MnO₂ electrode had decreased to ~0.7 V vs. Hg/HgO. The MnO₂ cathode with 60 mg/cm² loading was mechanically milled for 50 h.

The discharge capacity of MnO₂ electrode was 220 mAh/g, which was much smaller than the discharge capacity of the same alloy electrode in 6 M KOH electrolytes at a cycling current of 50 mA/g. The MnO₂ cathode in 6 M KOH electrolytes at a cycling current of 50 mA/g.

Charge/discharge performance of LmNi₄.₁Co₀.₄Mn₀.₄Al₀.₃ as battery anode and cathode.—To compare the performance of MH/MnO₂ AFC after interruption of the supply of reactants with the battery behavior, the electrochemical charge/discharge properties of MH and MnO₂ electrode in 6 M KOH were investigated. Figure 6 shows the charge/discharge behavior and cycling performance of an LmNi₄.₁Co₀.₄Mn₀.₄Al₀.₃ anode under these conditions. As previously stated, the discharge capacity at 50 mA/g was around 250 mAh/g, which was much smaller than the discharge capacity of the same electrode in the FC. The change in potential as a function of discharge capacity (discharge time × 50 mA/g) under battery conditions (Fig. 6a) was similar to that of the same alloy under AFC conditions with no hydrogen supply (Fig. 4). The LmNi₄.₁Co₀.₄Mn₀.₄Al₀.₃ anode showed very stable charge/discharge behavior under battery conditions and did not require initial activation (Fig. 6b) because the material was mechanically milled for 30 min before electrode preparation.

Figure 7a shows the discharge/charge behavior of MnO₂ cathodes in 6 M KOH electrolytes at a cycling current of 50 mA/g. The discharge behavior of MnO₂ electrode shows two potential plateaus. The discharge capacity of MnO₂ electrode was ca. 220 mAh/g.
which was also much smaller than that of a same MnO2 cathode with a 100 mg/cm2 MnO2 loading (~630 mAh/g) under AFC conditions with no oxygen supply (Fig. 4). The capacity of the MnO2 cathode under FC conditions at potentials below −0.4 V was similar to that of similar MnO2 cathodes under battery conditions (Fig. 4). Therefore, the capacity of MnO2 cathode at potential around −0.1 V under AFC conditions with no oxygen supply (Fig. 4) was due possibly to the large amount of oxygen remaining in the channels and tube when the oxygen is shut off.

To fully use the energy stored in MnO2, the AFC cathode should normally operate at potentials slightly above that of the MnO2 plateau, allowing it to go below the plateau when high power output is needed. If the normal operating voltage of the FC is 0.6 V, and potential of MH anode is at −0.8 to −0.85 V (Hg/HgO), the plateau potential of cathode around −0.2 to −0.25 V (Hg/HgO). However, the actual MnO2 plateau potential is about −0.4 V (Hg/HgO). Modifying MnO2 by doping or by mixing it with small amounts of Ni(OH)2 can increase its plateau potential. However, incorporation of 10 wt% Ni(OH)2 was shown to decrease the electrocatalytic activity for oxygen reduction. In addition, mechanically-milled MnO2 has higher charge/discharge cycling stability because the improved conduction pathways between it and graphite are effective in suppressing the formation of electrochemically inactive Mn3O4 under deep discharge conditions. Accumulation of Mn3O4 during repeated charge/discharge cycling causes capacity decline of the MnO2 cathode. Although the addition of bismuth oxide can effectively suppress Mn3O4 formation and increase the cycling stability of MnO2 in alkaline electrolytes, slightly soluble bismuthite ion may move to the anode where it may be deposited as bismuth, decreasing the electrocatalytic activity of MH for hydrogen absorption. A mechanically milled bismuth-free MnO2 AFC cathode showed a reasonable cycling stability because it normally operated in the potential range between −0.1 to −0.4 V (Hg/HgO), higher than the Mn3O4 formation of −0.5 V (Hg/HgO).7 Figure 7b shows the excellent cycling stability of mechanically milled MnO2 during charge/discharge cycling between +0.2 and −0.2 V (Hg/HgO). However, the potential of the MnO2 cathode may decrease below −0.5 V at very high peak power demands, which could result in possible formation of Mn3O4 and would concurrently result in a low cycling stability. In this case, a separate Ni/MH or Li-ion battery may still provide better power assistance to the FC, as both devices are optimized.

**EIS measurement of MH/MnO2 and Pt AFCs.**—The MH/MnO2 FC can be considered as a combination of a conventional AFC and a MH/MnO2 secondary cell. These differences can be quantified by electrochemical impedance spectroscopy. Figure 8 shows the imped-
Figures 9. Impedance spectra of MH and Pt AFC anodes at different potentials. The numbers in the plots indicate the frequency. MnO$_2$ loading: 60 mg/cm$^2$. Pt loading, as Fig. 8.

Figure 8. Impedance spectra of MH and Pt AFC anodes at different potentials. MH anode loading: 60 mg/cm$^2$ + 0.3 mg/cm$^2$ Pt, Pt catalyst loading: 0.3 mg/cm$^2$.

The charge-transfer impedance of the MnO$_2$ electrode with state loading was similar to that of the Pt cathode with 0.3 mg/cm$^2$ loading when the electrode potential was higher than $\sim$0.150 V. However the high-frequency semicircle for MnO$_2$ was larger than that for Pt, which may possibly be attributed to the high loading of MnO$_2$, a poor electronic conductor. Increasing the electronic conductivity of the MnO$_2$ cathode is expected to improve its electrochemical performance for oxygen reduction.

Conclusions

MH alloy (MH, LmNi$_{4.1}$Co$_{0.4}$Mn$_{0.4}$Al$_{0.3}$) and MnO$_2$ have been used successfully as electrocatalysts for hydrogen oxidation and oxygen reduction in an AFC. Its steady-state power output with high catalyst loading ($>$150 mg/cm$^2$ at anode and cathode) was comparable to that of carbon-supported platinum AFC with 0.3 mg/cm$^2$ loading at the anode and cathode. However, the MH/MnO$_2$ AFC delivered additional power when the cell voltage was stepped from normal operation voltage to a lower value because MH and MnO$_2$ not only act as electrocatalysts but also as energy storage as in a secondary cell. The MH and MnO$_2$ anode and cathode were quickly recharged by gaseous hydrogen and oxygen. During charging, the cell voltage returned to its normal value. Other advantages of the MH/MnO$_2$ AFC are its potentially low cost and the fact that it can be recharged by gaseous hydrogen and oxygen. During charging, the cell voltage returned to its normal value. Other advantages of the MH/MnO$_2$ AFC are its potentially low cost and the fact that it can be recharged by gaseous hydrogen and oxygen.

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