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Single Cell Performance Studies on the Fe/Cr Redox Energy Storage System Using Mixed Reactant Solutions at Elevated Temperature

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Eighteenth Intersociety Energy Conversion Engineering Conference
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Experimental studies in a 14.5 cm² single cell system using mixed reactant solutions at 650°C are described. Systems were tested under isothermal conditions, i.e., reactants and the cell were at the same temperature. Charging and discharging performance were evaluated by measuring watt-hour and coulombic efficiencies, voltage-current relationships, hydrogen evolution and membrane resistivity. Watt-hour efficiencies ranged from 86% at 43 mA/cm² to 75% at 129 mA/cm² with corresponding coulombic efficiencies of 92% and 97%, respectively. Hydrogen evolution was less than 1% of the charge coulombic capacity during charge-discharge cycling. Bismuth and bismuth-lead catalyzed chromium electrodes maintained reversible performance and low hydrogen evolution under normal and adverse cycling conditions. Reblending of the anode and cathode solutions was successfully demonstrated to compensate for osmotic volume changes. Improved performance was obtained with mixed reactant systems in comparison to the unmixed reactant systems.

INTRODUCTION

Various electrochemical concepts are being pursued as methods for bulk electrical energy storage. The NASA Fe/Cr Redox Energy Storage System (1) continues to be an attractive system because it uses soluble redox couples and has unique design flexibility (2). Technology development work, since its inception, has focused on room temperature operation and maintaining a high degree of reactant solution separation. Membrane development has focused on achieving low iron and chromium cross-diffusion rates while maintaining high counter-ion transport. In the past seven years significant advances have been made in membrane properties at room temperature which have improved the overall system performance (3).

Recent system development work, however, has focused on elevated temperature operation for two reasons. First, large, multiecell systems will be exothermic due to electrochemical inefficiency and resistive losses during cycling. This heat will maintain the system at elevated temperature and any waste heat can be rejected more economically through heat exchangers at the higher system operating temperatures. Second, improved charging performance has been attained at elevated temperatures due to a change in the chromium solution chemistry (4). At room temperature the acidified chromium chloride solution contains approximately equal concentrations of an electrochemically active species, Cr(H₂O)₅Cl²⁺, and the electrochemically inactive species, Cr(H₂O)₆³⁺ (5). Charging performance at room temperature beyond 50% state-of-charge is slow because of the slow rate of reequilibration between the inactive and the active species. However, at elevated temperature a shift in the chemical equilibrium occurs from the inactive Cr(H₂O)₆³⁺ species to the active Cr(H₂O)₅Cl²⁺ species and the rate of equilibration increases. Associated with the equilibrium shift is improved charging rates of the system up to levels greater than 90% state-of-charge.

System operation at elevated temperature, however, has significantly reduced the ionic selectivity of the membranes developed for room temperature application. Crossmixing rates of the iron and chromium reactants become significantly greater so that the reactants approach equimolar conditions much faster at elevated temperature than at room temperature. As a result, recent studies have been directed toward a mixed-reactant concept.

The use of mixed reactant solutions has several advantages when compared to unmixed reactants. (The basic trade-off in using mixed reactants is that a high current efficiency is sacrificed for an improved voltage efficiency. Trade-off of current efficiency and voltage efficiency to attain maximum watt-hour efficiency will depend on membrane properties and system operating parameters.) The major advantage is that a highly permselective membrane is not required. The less-selective membrane types are readily available and are also considerably less costly. Solution volume changes arising from osmotic pressure differences between the two reactants could also be corrected by remixing of discharged reactants. Another advantage is that chemical production costs from chromite ore could be lower than the manufacture of pure chemicals since separation of the iron and chromium would be unnecessary. Lastly, stack costs, resulting from smaller stack sizes, could be reduced as a result of the lower cell resistivity and higher power.
Disadvantages of using mixed reactants, in addition to the lower coulombic efficiency, are that greater quantities of reactants are required and the open-circuit voltage is reduced. Reactant quantities are only increased by 50% because an allowance for crossmixing is no longer required. Recent studies of Redox chemicals production costs (6, 7) have shown that chemical costs can be reduced significantly and that it is economically feasible to use the additional reactant required.

Experimental studies in a 14.5 cm\(^2\) single-cell using mixed reactant solutions at 65\(\degree\)C are described. Systems were tested under isothermal conditions, i.e., reactants and the cell were at the same temperature. Charging and discharging performances were evaluated by measuring watt-hour and coulombic efficiencies, voltage-current relationships, hydrogen evolution and membrane resistivity. Several catalysts were also evaluated for negative electrode performance. Performance comparisons are made on mixed and unmixed reactant systems at room and elevated temperatures.

EXPERIMENTAL

A schematic diagram of the hydraulic and electrical components of the system is shown in Figure 1. A schematic diagram of the 14.5 cm\(^2\) cell components is shown in Figure 2.

Watt-hour determinations were obtained by integrating the voltage-time relationships for constant current charge-discharge cycles. Coulombic efficiency was determined directly from the current-time integrators. Hydrogen evolved from the negative electrode was measured volumetrically with a gas trap. Cell and membrane resistivities were measured with a 1 KHz impedance bridge. Electrode kinetics, stability and flexibility were evaluated by determining the cell voltage-current relationship for short-term (approx. 15 seconds) charges and discharges.

RESULTS AND DISCUSSION

System Comparisons - System operation at elevated temperature has significantly improved the cell charging and discharging performance. Excellent charging characteristics for both unmixed and mixed reactants were achieved up to levels greater than 90% state-of-charge as a result of the shift in the chromium solution species equilibrium. A comparison of constant current charging performance at room temperature and both 60\(\degree\)C and 65\(\degree\)C for the two reactant types is shown in Figure 3. Differences in current density and internal resistance of the various cells have little effect on performance in comparison to the effect of increased temperature. Discharge performance as a function of temperature is only affected by the internal resistance of the cell. The same chromium species, Cr(H\(_2\)O)\(_5\)Cl\(^+\), is present in the charged solution regardless of temperature.
Charge and discharge performance comparisons were made from the voltage-current relationships for the mixed and unmixed reactant systems, both at room temperature and 65°C. Results at 50% state-of-charge are shown in Figure 4. The mixed reactant system with the less selective membrane has a much lower internal resistance and higher voltage efficiency than the other systems. Cell resistivity at 65°C and 50% state-of-charge for the mixed reactants with a ML-21* membrane is 0.87 ohm-cm² compared to 3.0 ohm-cm² for unmixed reactants with the more selective CDIL-AA5-LC** membrane. Higher discharge voltages are obtained below 20 mA/cm² for the unmixed reactants since the open-circuit voltages are higher. However, at current densities greater than 20 mA/cm², discharge voltages with unmixed reactants are higher due to the lower cell resistance.

The difference in open-circuit voltage between unmixed and mixed reactants as a function of state-of-charge at 30°C and 65°C, respectively, is shown in Figure 5. Open-circuit voltage for the mixed reactants at 65°C is about 50 millivolts lower than the unmixed reactants at 30°C between 20% and 90% state-of-charge. The lower open-circuit voltage is to be expected because of the thermodynamic and Nernstian effects of temperature and reactant concentration differences. Some experimental error in these results is anticipated because of uncertainty in determining the exact state-of-charge. These results, however, indicate the open-circuit voltage penalty associated with mixed reactants at 65°C.

Membrane Characteristics - Numerous high selectivity, anion transporting membranes designed for use with unmixed reactant systems were evaluated for ferric ion diffusion as a function of temperature. The increase in ferric ion transport in going from room temperature to 65°C for five membranes is shown in Figure 6. The selectivity loss, plus chemical incompatibility in some cases, made the concept of using highly selective membranes with unmixed reactants unworkable for the 65°C application. Replacement of the high selectivity anion membrane with a low selectivity cation membrane (ML-21) yielded membrane resistivities between 1.0 ohm-cm² and 0.3 ohm-cm² at 350°C and 650°C, respectively (Figure 7). Consequently, subsequent cell testing was performed using the ML-21 membrane in a mixed reactants system.

*Source. RAI Research Corporation, Hauppauge, L.I., NY 11786
**Source. Ionics, Incorporated, Watertown, MA 02172
The ML-21 membrane was evaluated under charge-discharge conditions in a standard Redox cell with mixed reactants. Cell watt-hour and ampere-hour efficiencies were measured by cycling at various constant currents in order to assess the relationship between the selectivity and resistivity for this particular membrane. Current efficiency is a measure of the membrane selectivity, i.e., higher selectivity yields a higher coulombic efficiency since crossmixing of the charged species is reduced. Higher current densities also give higher current efficiencies because the shorter cycle time results in less self-discharge due to crossmixing. Watt-hour efficiency takes into consideration the discharge/charge voltage efficiency which is a measure of the membrane resistivity, i.e., lower membrane resistivity leads to a higher voltage efficiency. Thus there is a maximum watt-hour efficiency for a particular membrane depending on the combined effect of its selectivity, resistivity, and the operating current density. Figure 8 graphically displays the voltage/time relationship for a 64.6 ma/cm² current density cycle using the ML-21 membrane. Watt-hour and ampere-hour efficiencies at up to 73% state-of-charge for current densities of 43 ma/cm² to 129 ma/cm² are given in Table 1. Watt-hour efficiency ranged from 86% at 43 ma/cm² to 75% at 129 ma/cm², while current efficiency increased from 92% to 97%. The maximum watt-hour efficiency, though not specifically determined was greater than 86% at a current density less than 43 ma/cm². Only the ML-21 membrane has been characterized to date.

<table>
<thead>
<tr>
<th>Current density, ma/cm²</th>
<th>Cell resistance, ohm-cm²</th>
<th>Coulombic efficiency, percent</th>
<th>Watt-hour efficiency, percent</th>
<th>Hydrogen evolution, percent</th>
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<tr>
<td>43</td>
<td>0.74</td>
<td>92</td>
<td>86</td>
<td>0.3</td>
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<tr>
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<td>93</td>
<td>83</td>
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<td>95</td>
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<td>0.3</td>
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</tr>
<tr>
<td>129</td>
<td>0.94</td>
<td>97</td>
<td>75</td>
<td>.6</td>
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</tbody>
</table>

Cell area: 14.5 cm²
Membrane resistivity: 0.45-0.70 ohm-cm²
Membrane selectivity: 1000 mg Fe/100 ml/liter

Electrode Characteristics - The effect on cell performance of adding iron to the chromium solution is shown in Figure 9. The addition of 40% iron initially showed no change in the polarization test results and no increase in hydrogen evolution, indicating the gold-lead catalyzed negative electrode remained reversible with a high hydrogen overvoltage. After 25 cycles cell resistance increased slightly causing a slight drop in cell performance. The constant slope of the voltage-current line indicated unchanged reversible electrode performance. These results indicated the Fe/Cr Redox system electrodes could be successfully operated in the mixed reactant mode.
Several alternate catalysts for the negative electrode have been studied for mixed solutions in addition to the standard gold and lead (8) combination used with unmixed reactant systems. Alternate catalysts include: bismuth, bismuth-lead and silver-lead. All catalysts except silver-lead gave reversible electrode performance at current densities up to 129 mA/cm² and hydrogen evolution rates less than 1% of the charge capacity. An example of the reversibility of the bismuth electrode at approximately 30%, 60% and 85% state-of-charge is shown in the polarization curves of Figure 10.

A full cycle was performed to 74% state-of-charge after which a full cycle with standard original polarity was run. Cell and electrode performance appeared unaffected by the polarity reversal. Electrode kinetics remained reversible and watt-hour and ampere-hour efficiencies were unchanged. Probably the most significant result was the low hydrogen evolution rate after reversal. Apparently good bismuth distribution on the carbon felt substrate was achieved regardless of cell polarity. This is an important factor at the system level since it is possible for a stack to become completely discharged, or for a cell or group of cells in the stack to be discharged to a negative voltage and still retain good cell performance.

A second test to evaluate electrode flexibility was exposure of the bismuth-catalyzed electrode to air after normal cycling, drying in air and then return of the electrode to the cell. Polarization results are shown in Figure 12 after air exposure with no catalyst present, and after air exposure with catalyst added. The electrode performance after recatalyzation was unaffected by the air exposure. Performance without the added catalyst is not reversible.

### Additional In-depth Experimental Evaluation

Results from a polarity reversal test are shown in Figure 11 and Table II. After a normal cycle, bismuth salt was added to the "iron" solution and the cell polarity was reversed to make the cathode the anode and the anode the cathode. Thus, bismuth was completely oxidized from the original negative electrode while also being deposited on the new negative electrode during charging. A full cycle was performed to 74% state-of-charge after which a full cycle with standard original polarity was run. Cell and electrode performance appeared unaffected by the polarity reversal. Electrode kinetics remained reversible and watt-hour and ampere-hour efficiencies were unchanged. Probably the most significant result was the low hydrogen evolution rate after reversal. Apparently good bismuth distribution on the carbon felt substrate was achieved regardless of cell polarity. This is an important factor at the system level since it is possible for a stack to become completely discharged, or for a cell or group of cells in the stack to be discharged to a negative voltage and still retain good cell performance.
Cycling and Solution Reblending - Extended cycling effects were determined on a bismuth-lead catalyzed system with mixed reactants. The initial reactants were 1M Fe/1M Cr/2N HCl. Considerable volume transfer from the "chromium" to the "iron" solution was observed. The acidity of both solutions was adjusted to 3N HCl. During further cycling the osmotic transfer direction was reversed but at a much lower rate. Volume differences were equalized by backmixing, or reblending, of the two solutions to equal volumes. Polarization results during cycling at the two acidities and after reblending the solutions three times are shown in Figure 13. No changes in cell performance were observed during 70 cycles.

CONCLUDING REMARKS

The current experimental investigation carried out in lab-size single cells has demonstrated the feasibility of using the mixed iron and chromium reactant Redox concept at elevated temperatures as a possible method for bulk electrical energy storage. Improved performance was achieved in comparison to the unmixed iron-chromium reactant system. Charging characteristics are improved at elevated temperature due to the presence of a higher proportion of the electrochemically active chromium species. Increasing operating temperatures and using a low selectivity, high conductivity membrane also yielded higher voltage and watt-hour efficiencies in spite of a lower coulombic efficiency.

The lower open-circuit voltage per cell for the mixed reactant system at elevated temperature is compensated for by the higher power output of each cell.

Electrochemically reversible performance was obtained with gold-lead, bismuth and bismuth-lead catalyzed negative electrodes. The negative electrode performance was unaffected by the equimolar quantity of iron in the solution. Reproducible performance was obtained with a bismuth catalyzed electrode regardless of cell polarity, exposure to air between cycles or remixing of the anode and cathode solutions.

REFERENCES