Lithium Ion Aqueous Cells

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Lithium ion aqueous cells were investigated using lithium intercalating compounds as anodes and cathodes. The aqueous electrolyte consisted of 4 to 5 molar solutions of either lithium perchlorate or lithium nitrate which contained lithium hydroxide in millimolar amounts to make the solutions slightly basic with a pH of about 8.5. Several electrode combinations were evaluated using lithium intercalating compounds such as lithium cobalt oxide and lithium manganese oxide as cathodes and lithium vanadium oxide, lithium manganese oxide, titanium disulfide, and molybdenum dioxide as the anodes. The cell employing manganese oxide as both the anode and cathode exhibited good charge-discharge characteristics with an open circuit potential of about one volt.
INTRODUCTION

Lithium ion or "rocking chair" cells have been extensively explored recently using organic solvent based electrolytes (1-5). The advantage of the lithium ion cell is that the safety problem associated with the cycling of metallic lithium, namely dendritic shorting, is eliminated. Lithium ion cell voltages and energy densities are comparable to lead-acid and nickel-cadmium cells with the additional advantage that their cell components are considered less hazardous to the environment. The primary drawback to the lithium ion cell development has been with the use of organic solvents in the electrolyte which are flammable. In addition, organic solvents offer no means for electrochemical protection of cells during overcharging operations (i.e., recombination in aqueous electrolytes), resulting in the need for costly electrical control circuits in multi-cell batteries.

Recently, it was discovered that lithium aqueous electrolytes could be successfully used in rechargeable cells containing lithium ion intercalating compounds as the anode and cathode (6,7). As reported, the aqueous lithium ion cell may offer the development of a safe, environmentally favorable rechargeable battery. The use of an aqueous electrolyte also allows for electrochemical overcharge protection of cells thereby making it a potentially lower cost cell for development into batteries. In view of these advantages, several electrode combinations were explored for lithium ion aqueous cells, and results are summarized in this report.

A lithium ion aqueous cell contains transition metal oxide electrodes which are chemically stable in the aqueous electrolyte provided the electrolyte pH is slightly basic (~pH>8). Additionally, the electrochemical potential of many of these oxides are between that of the hydrogen and oxygen evolution potentials, making them suitable for use in an aqueous cell. Lithiated metal oxides such as LiCoO₂, LiMn₂O₄, and LiNiO₂ can be used as positive electrodes which act as a source of lithium ions. Negative electrodes can use metal oxides such as VO₂, V₆O₁₃, and LiMn₂O₄ which then intercalate the lithium. The aqueous electrolyte typically consists of neutral pH lithium salts such as LiNO₃ and LiClO₄ in high concentrations (i.e., up to 5M). Lithium hydroxide is added to the electrolyte in millimolar concentrations in order to adjust the electrolyte pH to be slightly basic (pH~8). By keeping the pH slightly basic the hydrogen and oxygen evolution potentials are shifted, thereby allowing cell potentials up to about 2V. Cells are prepared cathode limited so that hydrogen evolution is minimized at the anode, thereby avoiding excessive irreversible reduction of the oxide anode material. At the end of charge, oxygen evolution occurs at the cathode and is considered controllable through gas recombination back into the electrolyte. A typical aqueous lithium ion cell that was studied, may be represented as:

\[ \text{(-)} \quad \text{V}_6\text{O}_{13} / 4\text{M LiClO}_4 + 1\text{mM LiOH} / \text{LiCoO}_2 \quad \text{(+) } \]

The cells are assembled in the discharged state, where, during charge, lithium ions are deintercalated from the LiCoO₂ cathode electrode and intercalated into the vanadium oxide electrode. The electrode processes are reversed during discharge. The cell reactions may be represented as:
\[
6\text{LiCoO}_2 + V_{6}\text{O}_{13} \xrightarrow{\text{charge}} 6\text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x V_{6}\text{O}_{13}
\]

The charged cell potential is 1.6 V resulting in a theoretical energy density of 234 Wh/kg, which is comparable to lead-acid and nickel-cadmium cells.

**EXPERIMENTAL**

Aqueous lithium ion cell electrodes were prepared by roll pressing composite pastes having compositions of 80 wt% active material, 10 wt% graphite powder, and 10 wt% Teflon powder binder onto platinum screen. Distilled water was used to prepare the electrode pastes for roll pressing. Electrodes having geometric areas of 1 to 1.5 cm² were air dried at 110°C and assembled as cells using a single layer of Celgard 2402 polypropylene separator. Carbon black (Black Pearls 2000) was attempted as a substitute for graphite in order to gain increased electrode porosity; however, the cathodes when oxidized evolved gas and leached a brown color into the electrolyte solution. The brown color and gas are probably due to humic acid formation and carbon dioxide evolution (8). Cells were immersed in argon gas deaerated aqueous electrolytes of 5M LiNO₃ -1mM LiOH (pH≈8.5) and cycled under constant current conditions at ambient temperatures. Cells were charged at a current density of 1 mA/cm² and electrode potentials measured versus a reference electrode. A hydrogen reference was used in the LiMn₂O₄/LiMn₂O₄ cell. Other cells used a LiCoO₂ pseudo-reference electrode which was found to have an equivalent potential to a saturated calomel electrode in the 5M LiNO₃ -1mM LiOH at 25°C. Table 1 lists the aqueous ion cells that were studied; included are the theoretical cell potentials and energy densities based on 100% utilization of the active materials. All cells were prepared cathode limited to avoid hydrogen evolution during charging.

The aqueous electrolytes 5M LiNO₃ -1mM LiOH (pH=8.2) and 4M LiClO₄ -1mM LiOH (pH=9.0) were studied by cyclic voltammetry using a smooth platinum working electrode versus a LiCoO₂ pseudo-reference electrode. Solutions were deaerated using argon gas prior to performing scans.

X-ray powder diffraction results were obtained using a Phillips PW 1729 X-ray generator. Diffraction patterns were verified versus JCPD standards. Electrolyte conductivities were measured using a Wayne Kerr model 6425 precision bridge at 1 KHz using Jones type conductivity cells calibrated using standard KCl solution. Cell cycling was performed using an AMEL model 545 galvanostat-electrometer and data collected using a Nicolet 310 oscilloscope.

**RESULTS AND DISCUSSION**

Figure 1 shows cyclic voltammograms obtained in 5M LiNO₃ -1mM LiOH (pH=8.2) and 4M LiClO₄ -1mM LiOH (pH=9.0) solutions at smooth platinum working electrodes using a
### TABLE 1. Aqueous Ion Cells Studied.

<table>
<thead>
<tr>
<th>Electrode Active Materials (-)</th>
<th>Theoretical Cell Potentials, V</th>
<th>Theoretical Energy Density, Wh/kg</th>
<th>Observed Avg. Cell Potential at 1 mA/cm² Load</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMn₂O₄</td>
<td>LiMn₂O₄</td>
<td>1.0</td>
<td>74</td>
</tr>
<tr>
<td>LiMn₂O₄</td>
<td>LiCoO₂</td>
<td>0.9</td>
<td>86</td>
</tr>
<tr>
<td>TiS₂</td>
<td>LiCoO₂</td>
<td>1.8</td>
<td>230</td>
</tr>
<tr>
<td>V₆O₁₃</td>
<td>LiCoO₂</td>
<td>1.6</td>
<td>234</td>
</tr>
<tr>
<td>MoO₂</td>
<td>LiCoO₂</td>
<td>2.4</td>
<td>285</td>
</tr>
<tr>
<td>CuO</td>
<td>LiMn₂O₄</td>
<td>1.8</td>
<td>323</td>
</tr>
</tbody>
</table>

* at 0.5 mA/cm²

### TABLE 2. LiMn₂O₄ X-ray Diffraction Results.

<table>
<thead>
<tr>
<th>LiMn₂O₄, [ASTM]</th>
<th>&quot;LiMn₂O₄&quot; Foote Mineral as Received</th>
<th>&quot;LiMn₂O₄&quot; Electrode Mix Processed With H₂O</th>
<th>&quot;LiMn₂O₄&quot; Cycled Electrode From Aqueous Cell</th>
</tr>
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<tbody>
<tr>
<td>(h,k,l)</td>
<td>d</td>
<td>I</td>
<td>d-observed</td>
</tr>
<tr>
<td>111</td>
<td>4.72</td>
<td>100</td>
<td>4.69</td>
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<tr>
<td>311</td>
<td>2.47</td>
<td>90</td>
<td>2.47</td>
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<tr>
<td>222</td>
<td>2.37</td>
<td>5</td>
<td>2.37</td>
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<td>400</td>
<td>2.05</td>
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<tr>
<td>331</td>
<td>1.88</td>
<td>10</td>
<td>1.88</td>
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<tr>
<td>333,511</td>
<td>1.58</td>
<td>50</td>
<td>1.58</td>
</tr>
<tr>
<td>440</td>
<td>1.45</td>
<td>90</td>
<td>1.45</td>
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<tr>
<td>531</td>
<td>1.39</td>
<td>30</td>
<td>1.39</td>
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<tr>
<td>533</td>
<td>1.25</td>
<td>10</td>
<td>-----</td>
</tr>
<tr>
<td>622</td>
<td>1.24</td>
<td>5</td>
<td>-----</td>
</tr>
</tbody>
</table>

Structure Determined From
Shift in d-spacing:

\[ [\text{Li}_{0.8}\text{Mn}_2\text{O}_4] \quad [\text{Li}_{0.75}\text{Mn}_2\text{O}_4] \quad [\alpha-\text{MnO}_2] \]
LiCoO$_2$ pseudo-reference electrode. Scans were performed between the hydrogen and oxygen evolution potentials at a scan rate of 50 mV/sec. Observed oxidation and reduction peaks corresponded to those typically observed at smooth platinum electrodes in aqueous electrolytes. Lithium perchlorate solutions were oxidized at about 0.9 V versus the LiCoO$_2$ reference. The lithium nitrate solution was found to possess a higher oxidation potential to about 1.2 V versus the reference and was the preferred electrolyte for use in the cell studies. The specific conductivity of the 5M LiNO$_3$ -1mM LiOH solution was measured to be 0.145 S/cm at 25°C.

Figure 2 presents the observed potential ranges of the lithium intercalation electrodes versus a LiCoO$_2$ pseudo-reference electrode. Table 1 depicts the average discharge potentials observed for 1 mA/cm$^2$ constant current discharges to a zero volt cell cutoff. Cells observed to have average discharge potentials lower than those expected from the theoretical cell potentials were not found to be stable in the aqueous electrolyte. The cell which used MoO$_3$ as the anode could not be cycled since the potential for lithium intercalation in MoO$_3$ was found to be below that of hydrogen evolution. Titanium disulfide was capable of intercalating lithium on charging; however, it rapidly decomposed in the electrolyte during discharge.

Figure 3 depicts the initial cycle of the LiMn$_2$O$_4$/LiMn$_2$O$_4$ cell at 1 mA/cm$^2$. The cell was charged to a cell cutoff voltage of 1.3 V to give a charge capacity of 0.5 F/mole of LiMn$_2$O$_4$. The cathode potential was measured versus a hydrogen reference and was found to remain below the oxygen evolution potential during charging. The observed capacity for the initial discharge to 0 V was 0.34 F/mole of LiMn$_2$O$_4$ with an average cell potential of 1.0 V. Subsequent cycles between a cell voltage of 1.3 V and 0 V resulted in discharge capacities of only 0.2 F/mole of LiMn$_2$O$_4$. The average cell potential during discharge remained at 1.0 V over ten cycles. The cell leads were then reversed and constant current cycling resumed between the cell voltage limits of 1.3 V and 0 V. Figure 4 shows the initial cycle for the reversed LiMn$_2$O$_4$/LiMn$_2$O$_4$ cell. The observed cell capacity and average discharge cell potential of the reversed cell was the same as for the original configuration. No capacity recovery over the 0.2 F/mole of LiMn$_2$O$_4$ observed for the initial cell configuration was obtained. The loss of expected capacity was believed to be due to a reaction between the lithium in the electrodes and the electrolyte to form LiOH. However, the electrolyte pH before and after cycling was found to be unchanged, suggesting that possibly the electrode preparation may have caused the lithium loss. To determine this, X-ray powder diffraction was performed on the pure LiMn$_2$O$_4$ and both the freshly prepared and the cycled LiMn$_2$O$_4$ electrodes. From table 2, the diffraction results show that the initial LiMn$_2$O$_4$ used was not fully lithiated as expected. A composition of only about Li$_{0.9}$Mn$_2$O$_4$ was determined from the observed diffraction peak shifts. The composition of the fresh manganese oxide electrode was Li$_{0.5}$Mn$_2$O$_4$, confirming a reactivity with water. A Li$_{0.7}$Mn$_2$O$_4$ electrode was used as the cathode in a cell and, after twenty cycles, disassembled in the reduced state. The X-ray pattern showed that the active material was completely converted to alpha-MnO$_2$. This corresponds to the phase changes observed by Thackery (5), where excessive lithium removal during oxidation results in the conversion of the LiMn$_2$O$_4$ phase to alpha-MnO$_2$. As a result of the electrodes being lithium poor, only about 0.2 - 0.3 F/mole of LiMn$_2$O$_4$ could be reversibly obtained at a current density of 1 mA/cm$^2$. Since excessive lithium removal can occur before oxygen evolution, cells of this type will require electrical overcharge.
Figure 1. Cyclic voltammogram of aqueous electrolytes at a smooth Platinum electrode.
Figure 2. Observed potential ranges in 5M lithium nitrate, 1mM LiOH (pH=8.2).
Figure 3. Initial cycle of manganese oxide cell.
Figure 4. Initial cycle of reversed manganese oxide cell.
(dotted line: anode versus lithium cobalt oxide reference)
(solid line: cell)
Li$_x$V$_6$O$_{13}$/5M LiNO$_3$–1mM LiOH in $H_2O/Li_{1-x}CoO_2$

![Graph showing cell potential vs. time]

Figure 5. Initial cycle of vanadium oxide/cobalt oxide cell.
Figure 6. Initial cycle of cupric oxide/manganese oxide cell.
protection and may not be able to rely on the chemical gas recombination mechanism used in other aqueous cells.

Figure 5 shows the initial cycling of the \( \text{V}_6\text{O}_{13}/\text{LiCoO}_2 \) cell at 1 mA/cm\(^2\). The initial cell open circuit potential was -0.15 V. The cell was charged to a cell voltage limit of 1.9 V to give a charge capacity of 0.35 F/mole of LiCoO\(_2\). The observed discharge capacity was only 0.19 F/mole of LiCoO\(_2\) with an average discharge potential of 1.19 V. \( \text{V}_6\text{O}_{13} \) was found to undergo lithium ion intercalation; however, it was slightly soluble in the electrolyte and the electrode capacity faded rapidly over five cycles. Excessive oxidation of the LiCoO\(_2\) cathode resulted in rapid capacity loss with cycling, similar to that observed with LiMn\(_2\)O\(_4\).

Figure 6 shows the initial cycle of the CuO/LiMn\(_2\)O\(_4\) cell at 0.5 mA/cm\(^2\). The initial cell open circuit potential was 0.10 V. Cupric oxide did not cycle as an anode and was not found to undergo lithium ion intercalation. Instead, the cupric oxide was converted to a soluble copper compound as noted by a blue color which was observed at the anode during the initial cycle. During the early stages of charging, a potential spike was observed as shown in figure 6; however, though it occurred at the anode, the reaction could not be identified. The observed discharge capacity, after charging to 1.6 V to a capacity limit of 0.4 F/mole of LiMn\(_2\)O\(_4\), was 0.05 F/mole of LiMn\(_2\)O\(_4\). The average cell potential during discharge was 0.69 V.

CONCLUSIONS

Li et al. (7) reported good cycling results with the use of an anode of VO\(_2\) (B) and the LiMn\(_2\)O\(_4\) cathode. These cycling results were not observed with the cells chosen in this study. Of the cells studied, only LiCoO\(_2\)/LiMn\(_2\)O\(_4\) and LiMn\(_2\)O\(_4\)/LiMn\(_2\)O\(_4\) were found to be suitable for use in the 5M LiNO\(_3\) -1mM LiOH electrolyte. Their cell potentials however, are only about one volt, with less than practical energy densities. In addition, the lithiated manganese oxide was found to undergo lithium loss in water, however it was stable in the slightly basic electrolyte. The lithiated transition metal oxide cathodes decompose during excessive oxidation which occurs before oxygen evolution. This would eliminate the use of the oxygen-hydrogen recombination reaction which is beneficial in other aqueous cells for overcharge protection. Improvements in electrode processing to limit loss of lithium or in situ enrichment of the electrodes with lithium is needed to demonstrate higher cell capacities. Further work is needed to evaluate other electrode combinations to improve on the energy density of the aqueous lithium ion cell.

REFERENCES

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