Investigations of the Electrochemical Stability of Aqueous Electrolytes for Lithium Battery Applications

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The electrolytic stability windows of several aqueous electrolytes were investigated by a constant current method. The electrode potential range depended upon the value of the imposed current. The magnitude of this behavior varied with the salt solution, its concentration, and pH of the electrolyte. At a leakage current density of 50 $\mu A/cm^2$, a 5 M solution of $LiNO_3$ had an electrolytic window of 2.3 V, spanning from -0.55 to 1.75 V with respect to the standard hydrogen electrode. These results demonstrate the feasibility of operating lithium batteries at voltages appreciably above the theoretical decomposition voltage of water.
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Organic solvent electrolyte cells now dominate commercial lithium battery applications in which the major consideration is the specific energy. One reason for this is that positive electrodes with high potentials can be used in these electrolytes.

Pure water has a thermodynamic stability window of only 1.23 V, and it is generally expected that the voltage of aqueous electrolyte batteries would be limited to that value. However, some common aqueous electrolyte batteries have voltages that greatly exceed that limitation. Examples are the lead-acid and the hydride/"nickel" systems. Lead-acid cells operate at voltages between 2.0 and 2.15 V,[1-3] and hydrogen and oxygen do not begin to evolve until about 2.4 V.[4] Metal hydride/nickel cells operate at 1.34 V, and oxygen evolution does not begin before reaching 1.44 V.[5,6]

In lead-acid cells, it has been shown[1,3,4] that lead is covered by a dense corrosion film of electronically insulating but ionically conducting $PbSO_4$, across which there is a steep potential gradient. This is why lead electrodes exhibit such a high hydrogen evolution overvoltage in H_2SO_4. Likewise, the high oxygen evolution overvoltage observed in nickel electrodes in alkaline electrolytes is due to the presence of an electronically insulating but proton-conducting layer of $Ni(OH)_2$ on the surface in contact with the electrolyte.[5,6] These are both analogous to the presence of a solid electrolyte layer (SEI) in lithium-ion cells, which makes it possible to use negative electrodes at potentials beyond the stability range of the typical organic electrolytes.

The use of aqueous electrolytes in lithium battery systems was pioneered by the Dahn group,[7-10] which demonstrated reversible cycling of $LiMn_2O_4$ and VO_2 in a lithium nitrate aqueous electrolyte. Many other articles have examined the behavior of lithium-reacting electrodes in aqueous electrolytes.[11-17] In these cases, however, the emphasis was on the behavior of the electrode reactants rather than on the electrolytes.

Aqueous electrolytes offer several important advantages when compared to those containing organic solvents. They are not flammable, and thus provide much better safety than electrolytes containing highly reducing organic species, which have been shown to vigorously react with the oxygen that evolves from some of the common positive electrode reactants at high potentials. In addition, both aqueous electrolytes and the separators used with them are much less expensive than those used in current commercial organic electrolyte cells. In general, aqueous salt solutions have very high ionic conductivities and should therefore be capable of very high power operation. Such behavior has been demonstrated with $LiCoO_2$.[17]

This work was undertaken to investigate the limits of the electrochemical stability of aqueous solutions and how it is affected by the identity and concentration of the salt present.

Experimental

A common technique used when evaluating the electrochemical behavior of an electrolyte is cyclic voltammetry. In this technique, a substantial and steady increase in the current at high and low potentials signals the onset of reactions involving the electrolyte. However, the apparent potentials at which reactions involving the electrolyte can vary with the scan rate, and there is sometimes an initial, gradual increase in the current. Details of such observations can be difficult to reproduce.

Batteries are operated at or near relatively constant potentials, and when they are charged, sit near their maximum operating potentials. Hence, steady-state measurements, rather than scanning measurements, are more appropriate when evaluating the electrochemical stability of electrolytes for use in battery applications. In the work described here, constant current measurements, rather than constant potential measurements, were made, for the latter did not quickly reach steady-state values, allowing some of the electrolyte to evaporate and its composition to vary.

Constant current steps were applied to a flooded three-electrode cell containing platinum foil working electrode (WE) and counter electrode (CE), and a Ag/AgCl reference electrode (RE). The potentials reported here are with respect to the standard hydrogen electrode (SHE) potential. Before each measurement, the platinum foil was rinsed in acetone, followed by repeated washing in concentrated sulfuric acid and rinsing in deionized water. To maintain consistent current densities, all but 1 cm^2 of the platinum was masked with nitrile cellulose. The electrodes were immersed 1 cm apart in aqueous solutions with the RE between them. Current steps were maintained for 1 h, after which the potentials of the electrodes had equilibrated in all cases. The potentials of both the WE and CE were recorded with respect to the RE, allowing the full cell (FC) voltage to be determined.

Aqueous electrolyte solutions of two salts, lithium nitrate and lithium sulfate, were prepared from commercial salts (Aldrich). Most of the studies related to aqueous lithium batteries have used one or the other of these. In addition, a few experiments were undertaken using lithium perchlorate, lithium chloride, and various alkali metal nitrates. All salt solutions had a neutral pH except when the pH was deliberately controlled using nitric acid or lithium hydroxide. Experiments on these salt solutions allowed evaluation of the effects of current density, salt identity, solution composition, and pH on the range of electrolyte stability.

Experimental Results

As anticipated, increasing the current density yielded a higher apparent WE potential, a lower CE potential, and a greater FC voltage in all cases. Figure 1 shows this behavior for 5 M $LiNO_3$ and 2

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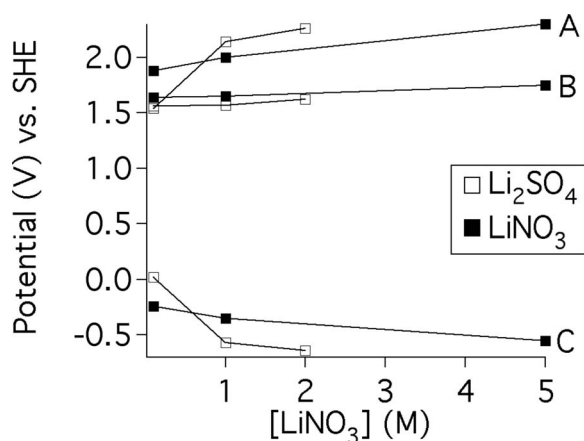z E-mail: rhuggins@stanford.edu; yicui@stanford.edu

Figure 1. (A) FC voltage and (B) WE and (C) CE potentials of Li_2SO_4 and $LiNO_3$ as a function of concentration at a current density of 50 $\mu A/cm^2$.

Figure 3. CE and WE potentials and FC voltage of 1 M $LiNO_3$ as a function of pH. pH was varied by adding HNO_3 or LiOH.

M Li_2SO_4, two electrolytes that have been used in aqueous lithium battery experiments. For 5 M $LiNO_3$ at a (low) current density of 50 $\mu A/cm^2$, the WE, CE, and FC potentials were 1.75, −0.55, and 2.30 V, respectively. There is a linear relationship between the potential and the logarithm of the current density for both salt solutions, as shown in Fig. 2. The 5 M $LiNO_3$ solution has a slightly wider total stability range than 2 M Li_2SO_4 at all current densities.

The location of the electrochemical stability range of pure water is pH-dependent, varying approximately 0.059 V per pH unit. The influence of pH upon the stability range was explored for the 1 M $LiNO_3$ solutions, which were prepared with pH values ranging from 0 to 14 by adding HNO_3 or LiOH to an initially neutral solution. The results are seen in Fig. 3.

To determine whether the observed increase in the electrochemical stability is unique to $LiNO_3$ and Li_2SO_4, experiments were also performed on 1 M $LiClO_4$, LiCl, $NaNO_3$, KNO_3, $Mg(NO_3)_2$, and 0.25 M $Ba(NO_3)_2$ under comparable conditions. Figures 4 and 5 show the stability windows of these lithium and nitrate salts, respectively, at 100 $\mu A/cm^2$.

Conclusions

A stepped constant current method was used to evaluate the electrolytic stability windows of several aqueous salt solutions by using platinum electrodes. The current density values used were comparable to those employed in many actual battery applications. All the
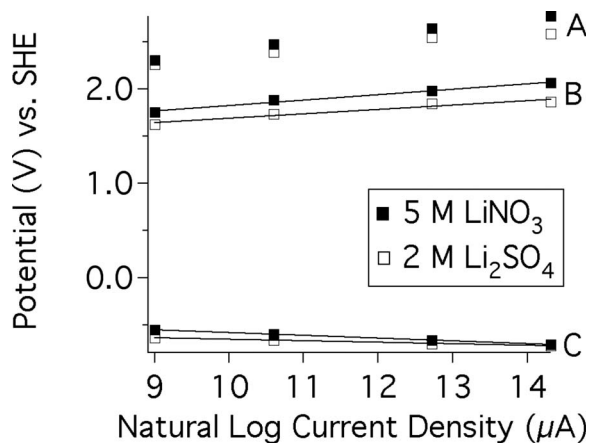
salt solutions investigated showed electrolytic ranges significantly greater than that expected for pure water. Concentrated $LiNO_3$ and Li_2SO_4, the most common aqueous lithium battery electrolytes used to date, showed similar stability ranges, approximately 2.3 V wide at a current density of 50 $\mu A/cm^2$. Other nitrate and lithium salt solutions showed similar behavior. The location of the stability win-

Figure 4. CE and WE potentials and FC voltage of (A) 1 M $LiNO_3$, (B) 1 M Li_2SO_4, (C) 1 M $LiClO_3$, and (D) 1 M LiCl at 100 $\mu A/cm^2$.

Figure 2. Semilogarithmic plots of the potential vs the current density of 5 M $LiNO_3$ and 2 M Li_2SO_4 showing (A) FC voltage, (B) WE potential, and (C) CE potential with their respective semilogarithmic best-fit functions.
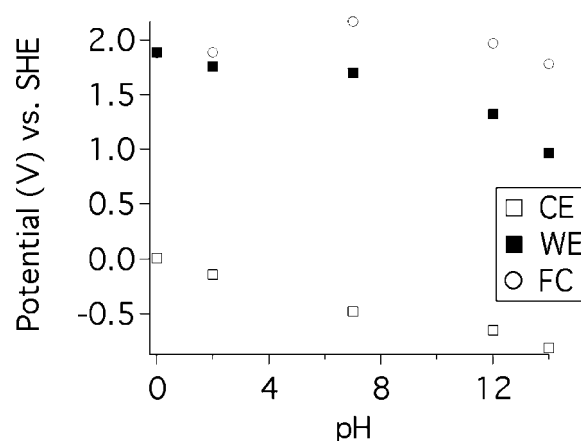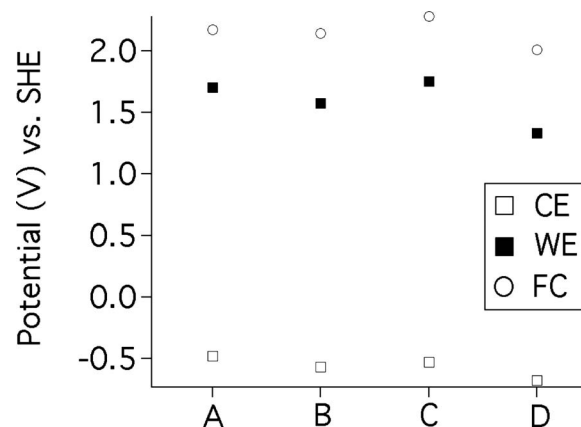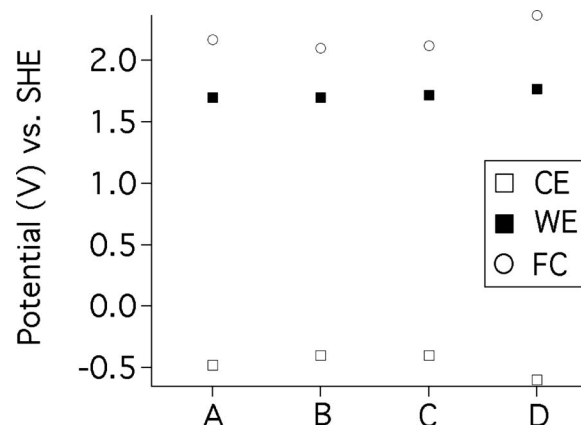

Figure 5. CE and WE potentials and FC voltage of (A) 1 M $LiNO_3$, (B) 1 M $NaNO_3$, (C) 1 M $Mg(NO_3)_2$, and (D) 0.25 M $Ba(NO_3)_2$.

dow of LiNO$_3$ generally decreased with respect to the SHE with increasing pH, and the width of the stability window was highest at neutral pH.

The span of the apparent electrolytic window depended upon the logarithm of the current density, so its practical value depends upon the magnitude of the leakage current that is permitted in a given application. This leakage current acts to cause self-discharge in any battery using such aqueous solutions as the electrolyte. The magnitude of this self-discharge depends upon the relationship between the electrode potentials and the stability limits of the electrolyte, and can have significant practical implications.

The authors do not know the reason for the observed extensions of the stability range of aqueous electrolytes and whether they reflect the local structure of the salt-containing water in the vicinity of the metallic electrodes or the formation of an SEI analog region.

The linear relationship between the logarithm of the leakage current and the potential is consistent with the empirical Tafel approximation of the general Butler–Volmer "activated complex" model of current transport across the "electron-transfer-limited region" of the electrolyte/electrode interface. It is also expected for a mechanism that involves minority electron or hole leakage through an electrolyte[18,19] and is observed in Hebb–Wagner experiments on minority electronic transport in solid electrolytes.[20] The same should be found in SEI layers.

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