

# High Voltage Alloys for Lithium Battery Cathodes

## Investigator

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## Abstract

The possibility of the use of selected metal and metal-metalloid alloys that have significantly lower weight than the transition metal oxide materials presently used in lithium-ion battery cathodes was experimentally investigated. In the course of this work the new concept of the use of hybrid electrolytes in aqueous electrolytes was developed. It was demonstrated that pairs of electrodes involving the insertion of different, rather than only the same, ions can be used in advanced batteries. This greatly broadens the choice of possible electrode materials, some with appreciably less weight. It was shown that the addition of certain salts makes it possible to extend the voltage stability range of aqueous electrolytes appreciably, even beyond that which is now used for high cycle life lithium-ion batteries with organic solvent electrolytes. The operation, and good kinetic properties, of the high potential lithium cathode material  $\text{Li}_x\text{CoO}_2$  in an aqueous electrolyte was demonstrated.

## Introduction

The initial objective of this project was to investigate the possibility of the use of selected metal and metal-metalloid alloys that have significantly lower weight than the transition metal oxide materials presently used in lithium battery cathodes in order to improve the specific energy of lithium-ion cells.

After the introduction of the concept of using hybrid-ion electrolytes, which allows the potential use of a much wider range of electrode reactants, the focus was changed to investigate the use of aqueous electrolytes in lithium-ion cells.

## Background

Lithium-ion cells are currently used in many applications in which high specific energy, the energy stored per unit weight, and high energy density, the energy per unit volume, are desired. An important constraint on the achievement of improved batteries of this type is the weight of the materials that are currently used in the electrodes, particularly in the positive electrode, the cathode.

However, essentially all current research activities aimed at the improvement of cathodes involve the investigation of transition metal oxide materials, in which the electrochemical reaction involves the redox behavior of the transition metals in the oxide crystal structure. Attention is mostly given to the possibility of the achievement of somewhat higher voltages, leading to greater energies. However, these materials are

inherently heavy, for their weight must include that of the several oxide ions as well as the transition metal reactants.

On the other hand, a number of materials have been used as electrodes in aqueous electrochemical cells that have significantly lighter weights for the same amount of charge.

It was decided to investigate some of these lighter materials, which are metal alloys, and also look at some metal-metalloid alloys, to see whether they will react at useful potentials, and with satisfactory kinetics, in lithium cells.

The issue is whether such host materials can be made to absorb lithium, rather than hydrogen. This has been shown to be the case for palladium, for it can react with a lot of lithium.

The metal hydrides currently used in battery anodes operate at electrical potentials that are close to the reversible hydrogen evolution potential in aqueous electrolytes, in order to provide the largest possible cell voltage. The hydrogen evolution potential in aqueous electrolytes is approximately 3 volts positive of the potential of elemental lithium. Therefore, the electronic band structure of alloys that accept hydrogen (or lithium) into their structures at that potential are such that they can act as 3 volt cathodes in lithium systems.

Especially interesting as potential lithium cathode materials are alloys that are known to absorb hydrogen at pressures much lower than one atmosphere. One prominent example is the group of beta titanium alloys, where approximately one hydrogen is absorbed at a pressure of about  $10^{-13}$  atmospheres. The Nernst equation relates the electrochemical potential to the hydrogen pressure, and shows that the potential is about 3.4 V vs the potential of pure lithium in this case. This would be a very convenient potential for a lithium cathode.

## Results

Initial experiments were undertaken to evaluate the behavior of boron-silicon alloys, beta titanium alloys containing Mn or Ni, and typical  $AB_2$  and  $AB_5$  metal hydride alloys as lithium-ion electrodes. On the whole, these were not very successful, for the reactions of these materials with lithium ions was sluggish.

This led to the concept of hybrid-ion electrolytes, in which two different ions are present in the electrolyte, one that reacts with the anode, and another that reacts with the cathode. This can be accomplished by using aqueous electrolytes if the potentials of both of the electrodes are within its stability range. This innovation promises to be very important, and a patent application related to it was prepared and submitted.

Experiments were performed on the properties of  $Li_xCoO_2$  electrodes, which are commonly used in commercial lithium-ion batteries, in an aqueous electrolyte. They

showed that excellent properties can be obtained, with potentials comparable to those typical of organic electrolyte cells, but at high rates, and with good cycle life.

Whereas the thermodynamic stability range of pure water is only 1.23 V, it was found that it is possible to use certain salts to greatly expand the useful voltage, to over 2.3 V. This is greater than the voltage of the lithium-ion cells that are currently being explored for use in safer and longer cycle life lithium-ion cells.

## **Conclusions**

This short program, which started out to explore the possibility of the use of metallic and metal-metalloid alloys that are typically used in aqueous electrolyte batteries in lithium-ion cells, evolved into a new direction as the result of the invention of the concept of hybrid-ion electrolytes. The potential utility of this approach for the development of safer, faster, less expensive and longer cycle life lithium batteries is very attractive.

## **Publications and Presentations Related to This Program**

### **Publications**

R. Ruffo, C. Wessells, R.A. Huggins, and Y. Cui, “Electrochemical behavior of  $\text{LiCoO}_2$  as aqueous lithium-ion battery electrodes”, *Electrochem. Comm.* 11, 247 (2009)

C. Wessells, F. La Mantia, R. Ruffo, R.A. Huggins, and Y. Cui, “Investigations of The Electrochemical Stability of Aqueous Electrolytes for Lithium Battery Applications”, *Electrochem. Solid State Letters* 13, A59 (2010)

### **Professional Society Presentations**

C. Wessells, R. Ruffo, R.A. Huggins, and Y. Cui, “Performance of  $\text{LiCoO}_2$  as Aqueous Lithium-ion Battery Electrodes”, presented at meeting of the Electrochemical Society, San Francisco, May, 2009

C. Wessells, F. La Mantia, R.A. Huggins, and Y. Cui, “Pursuing a Higher-Voltage Aqueous Lithium Battery” presented at meeting of the Electrochemical Society, Vancouver, April 25, 2010

### **Patent Application**

“Systems, Methods of Manufacture and Use Involving Lithium and/or Hydrogen for Energy-Storage Applications”, Provisional submitted April, 2009, Non-Provisional in April, 2010.

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