

Advanced FeF₃ Cathode Enabled Lithium-ion Battery

Za Johnson and Stephen Cordova
Mobile Energy Products, Inc.

G. G. Amatucci
Rutgers University

Copyright © 2008 SAE International

ABSTRACT

At present Li-ion batteries are the premier rechargeable energy storage technology and they offer a promising future as a power source for high energy density battery applications. Unfortunately, their high performance still falls short of energy density goals in many military ground battery and soldier portable applications. Although a number of factors within the battery cell contribute to this performance parameter, the most crucial one relates to how much energy can be stored in the positive and negative electrode materials of the lithium ion battery. Very little focus had been shown in the research of the electrochemistry of transition metal fluorides until Rutgers, The State University of New Jersey began its investigation. The reason for this apparent lack of interest in these compounds was that their intrinsic properties appeared to make them less desirable as possible electrode materials for lithium batteries. Metal fluorides are notorious for their poor electronic conductivity due to the large bandgap induced by the highly ionic character of the metal-halogen bond. This point had kept them away from the radar screen in the search for improved electrode materials for rechargeable lithium batteries. Iron-based compounds are of interest for batteries because of their low cost and low toxicity.

Amatucci and coworkers found that metal fluorides such as iron and bismuth fluorides can be fabricated as high capacity reversible cathodes for rechargeable lithium batteries by converting them into nanoscale electrode materials [1]. We have found that metal fluorides such as iron fluoride prepared with nanoscale particles are able to support appreciable electron conductivity and function as reversible electrodes in non-aqueous lithium ion batteries. The iron fluoride, FeF₃, in specially formulated nanoscale particles is able to support appreciable electron conductivity by the shortening of bulk path lengths and augmentation of electron tunneling. These nanocomposites can be prepared through a variety of methods which are practical on a large scale. Electro Energy has fabricated laboratory test cells from cathodes

prepared from a mixture of the metal fluoride and high surface carbon. The cell incorporates standard lithium ion battery separators and organic liquid electrolytes. The key technology is the nanocomposite cathode prepared by sophisticated methods which enable the composite electrode mixture, formed from slurry using a suitable solvent, and coating the electrode onto a substrate which is then dried and compacted to achieve the desired density for optimum electrochemical performance.

The paper summarizes the test results gathered from laboratory test cells fabricated from the FeF₃ cathode material. The cells were tested at various rates and temperatures and life cycle tested to characterize the capability of the cathode material to meet DoD application requirements. The greatest risk anticipated in the development of this technology is extending beyond the laboratory cell level into the large cell and battery level. In this regard, Electro Energy's wafer lithium cell is ideal for prototype cell development, the cells are easy to construct and initial cell development work can be done using single layer anodes and cathodes [2-5].

INTRODUCTION

SOLID ELECTROLYTE INTERFACE LAYER

A critical part of the early development of lithium ion cell chemistry was the characterization of the charge and discharge process and gaining information about the electrochemical reactions that occur. During the 1st charge of the formation process when the anode is charged for the first time lithium ions are intercalated into the carbon structure. In addition to the lithium intercalation several other electrochemical reactions take place during the next several cycles of the formation process. One of these is the decomposition of the electrolyte on the anode and the formation of a surface layer, often referred to as the solid electrolyte interface (SEI) layer. Without the SEI layer the lithium ion cell has a very short life because the SEI layer protects the carbon anode from continued reaction with the

electrolyte. The FeF_3 cell is significantly more complex than typical lithium ion cell chemistries. First of all the lithium required for the anode does not come from the cathode but must be introduced separately. Second the cathode stores energy chemically as well as by intercalating lithium ions. Finally, the structure of the cathode active material changes during charge and discharge. Because of these differences from typical lithium ion cells the properties and chemical composition of the SEI layer plays an especially critical role in the ability of the cathode and anode to cycle over an extended period of time.

ELECTROLYTE

In a complex system such as this the electrolyte plays a very important role in the stability of the cathode and anode. The electrolyte is made up of several components which include; a lithium salt dissolved in an organic solvent or mixture of solvents. Both the lithium salt and the composition and concentration of the solvents play important roles in the formation of the SEI layers and in the chemical reactions that affect the life of the lithium ion cell. For this reason Electro Energy has conducted several experiments to determine the effects of electrolyte composition and concentration on the performance of the FeF_3 lithium ion cell chemistry. Data from these experiments is presented below.

SEPARATOR

The separator which suspends the electrolyte and electrically isolates the anode and cathode also contributes to the performance of lithium ion cell. In the case of the FeF_3 lithium ion cell the separator thickness, porosity, pore size and pore tortuosity each contributes to the electrochemistry of the cell. It appears that because of the complex reactions that occur on the cathode surface these separator characteristics play an even more important role in the FeF_3 cell electrochemistry than in typical lithium ion cells. This paper presents data showing performance effects for several separators.

DEVELOPMENT APPROACH AND DISCUSSION

Each of the subjects outlined in the Introduction have been studied under various conditions to determine their effect on the performance of the FeF_3 lithium ion cell chemistry. The effects of each are presented in the following four areas of performance.

CHARGE & DISCHARGE

The FeF_3 lithium ion cell has two voltage regions on charge and discharge. One region involves the intercalation of lithium ions in the FeF_3 cathode and is similar to that of other lithium ion chemistries. The other region involves the conversion of Fe through its several valence states, which occurs because in addition to

energy storage in the intercalation step the FeF_3 stores energy in the chemical conversion step.

The voltages at which these two steps take place are distinct. Modeling and experimentation verify that on charge the conversion reactions take place first and are for practical purposes 100% complete before the intercalation step begins. The discharge steps correspond to those on charge. When discharged the cell completes the intercalation step at voltages similar to typical lithium ion cells. Additional energy is gained from a conversion step which occurs at a depressed voltage.

Figure 1 shows the FeF_3 charge curve as a function of specific capacity. The curve looks similar to typical Li-ion charge curves.

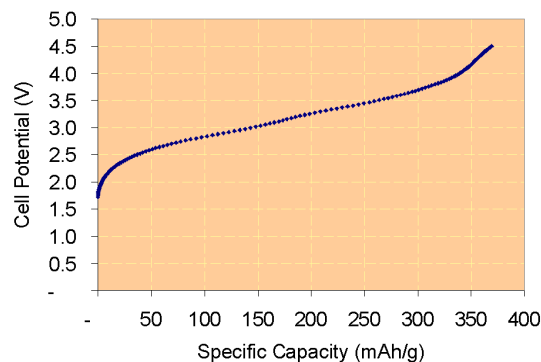


Figure 1 Charge Voltage versus Specific Capacity

Figure 2 shows the FeF_3 charge curve as a function of specific energy.

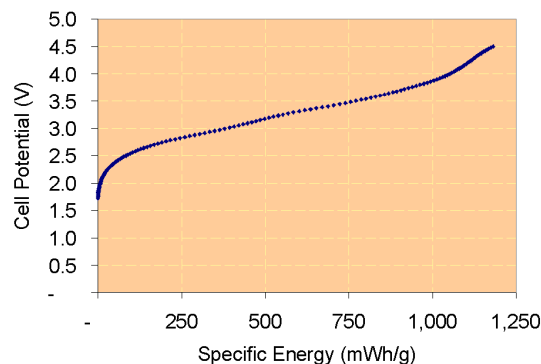


Figure 2 Charge Voltage versus Specific Energy

Figure 3 shows the FeF_3 discharge curve as a function of specific capacity. The curve demonstrates the change in the slope of the voltage as the cell discharge changes from intercalation to the conversion reaction. This change occurs around 2.1 volts. The curve shows that