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LiF dissolution by anion-binding-agents in Li-CF_x battery systems: Lower ohmic and interfacial resistance

G. Nagasubramanian, K. Fenton
2545 Power Sources Design and Development
Sandia National Laboratories
Ph: (505)-844-1684
Email: gnagasu@sandia.gov

Abstract:

In this paper we will discuss our preliminary thermal and electrochemical data aimed at developing a robust nonflammable Li-CF_x cell capable of wide temperature operation. To accomplish this goal, we are evaluating a thermally stable solvent comprised of an anion binding agent (ABA) and lithium fluoride (LiF), typically at a 1:1 molar ratio. In conventional carbonate based electrolytes, ABA is soluble while LiF remains insoluble. However, the neutral ABA solubilizes LiF and forms a salt complex represented as $Li^+(ABAF^-)$. We are exploiting this unique feature and apply this strategy to CF_x chemistry to improve cell performance, due to the CF_x cell chemistry generating LiF as discharge product. Continuous solvation of the salt mixture during discharge allows for utilization of electrolytes initially containing sub stoichiometric amount of LiF. The practical benefits are reduced cell weight, mitigation of electrode fouling, and consequently better low temperature performance. Electrolytes containing dimethyl methyl phosphonate (DMMP), 1M tris(pentafluorophenyl) borane (TPFB) and varying concentrations of LiF (1M; 0.5M and 0.1M) were prepared and characterized for ionic conductivity and voltage stability. In general, ionic conductivity decreases with decreasing LiF concentration. The room temperature conductivity for the DMMP 1M TPFB:1M LiF is ~ 9mS/cm and ~3mS/cm for the 1M TPFB:0.1M LiF. Unlike the conductivity, the electrochemical voltage stability did not vary substantially with LiF concentration and the electrolytes showed a stable voltage window in the range 0-3.5V vs. Li^+/Li, which is substantially wider than the Li-CF_x cell voltage. Flammability measurement performed at our thermal abuse facility demonstrated that the electrolyte was nonflammable. Discharge performance of CF_x materials obtained from several vendors was evaluated in 2032 coin cells at room temperature. Experimental results demonstrate a reduction in ohmic resistance and interfacial resistance during discharge for a cell containing lower concentrations of added LiF compared to ABA. These observations are a direct demonstration that the unbound ABA in the electrolyte dissolves the LiF generated in the discharge reaction.

Introduction

Discharge products for several of the commonly used primary battery chemistries, including $SOCl_2$, are currently classified as hazardous materials with low exposure limits[1]. The exposure limits for these materials vary, but are generally in the single ppm range. This excludes them for use in many applications, particularly when operator safety and proximity is a key consideration. This has inspired a renewed focus in development and exploration of other lithium primary batteries to substitute for those having chemical safety concerns. Demand for batteries with long life, lightweight, high-energy density and eco-friendly features are driving growth in identifying alternative chemistries. For our internal applications, the alternative chemistries should: 1) have long life and high capacity, 2) produce non-toxic discharge products, 3) perform over a wide temperature range and 4) be composed of thermally stable materials.

Lithium carbon monofluoride (Li CF_x) chemistry satisfies the first two criteria. However, like any other lithium chemistry, it is also stymied by solvent flammability problems and low temperature performance problems due to the fouling of the cathode pores by the discharge product. Improving these problems is central to the adoption of this chemistry. To overcome the two problems we are proposing to use: 1) a nonflammable solvent and 2) a thermally stable salt. Regarding cathode fouling, we are proposing an innovative approach where we add neutral anion binding agents (ABA) capable of dissolving the discharge product, which in this case is lithium fluoride (LiF), to the electrolyte and thus relieving or mitigating cathode fouling. By adding sub-stoichiometric amounts of LiF to the electrolyte containing excess amount of ABA dissolved beforehand, causing the solution to contain free Li^+ABAF^- salt complex and sufficient free non-complexed ABA for dissolving the discharge product. The principal goal of this approach is to show that cell performance can be enhanced by dissolving the discharge product in real time. This idea has far reaching impact beyond Li-CFx in improving battery performance of, say for example, rechargeable batteries like Li-O_2 and Li-ion batteries with conversion compounds that have potentially huge stored energy but suffer from voltage hysteresis and poor recharge capability[2]. The down side to this implementation is that the charge voltage can potentially be a lot higher than the discharge voltage, which amounts to expending more energy to recharge the battery. If an ABA can be identified that can dissolve the discharge product, for example, Li_2O_2 the reversibility and performance of the Li-O_2 battery can be vastly improved [3-5]. The same rationale is applicable for the conversion chemistry.

We are leveraging our understanding of and experience with ABAs and nonflammable solvents gained in our Li-ion research and applying the knowledge to this project[6-8]. We are evaluating DMMP solvent in conjunction with tris(pentafluorophenyl) borane (TPFB) bound to LiF. DMMP has been studied extensively by others as fire retardant in Li-ion cells[9-12]. Pairing DMMP with TPFB-LiF synergistically endows the cell chemistry with both enhanced thermal stability and improved electrochemical performance.

The propensity of the ABA to dissolve LiF has been taken advantage of for improving Li-ion cell performance before. For example McBreen proposed the use of ABAs, also known as anion receptors, to dissolve the accumulated LiF, due to the decomposition of the $LiPF_6$ salt, on cathode surface in Li-ion

batteries[13]. He demonstrated that the cathode can be rejuvenated by dissolving the LiF layer. West[14] *et.al.* have demonstrated reversible intercalation of F^- in graphite from an organic solution containing an ABA and LiF. However, our work focuses on dissolving the generated LiF in the Li-CFx discharge to improve the ohmic and interfacial resistances as the cell discharge. We are accomplishing these by varying the composition of the ABA-LiF complex salt in the electrolyte. In this paper we will discuss the thermal and the electrical properties of the DMMP/ABA-LiF electrolyte and the electrical performance of CFx materials obtained from different vendors in the above electrolyte.

Experimental

Several CF_x powders were obtained both through purchase and free from several vendors. Vendor identification is not included as it does not add to the discussion of the material behavior and electrolyte mechanisms. The materials are designated as A, B, C and D. The solvent DMMP (99.5% purity) was purchased from PFALTZ-Bauer and used as received, see Figure 1. The TPFB ABA (Figure 1) was synthesized by Richman Chemicals under a Sandia contract and the LiF was purchased from Fischer Scientific (>99.95 purity). The ABA, LiF, and CF_x were all used as received but were baked out under vacuum overnight at 110 °C before using. Three different electrolytes containing DMMP 1M TPFB and 1M LiF, 0.5M LiF or 0.1M LiF were prepared in an argon filled glove box. CFx electrodes were made as described elsewhere[15]. The electrode composition is 94:3:3 wt% (active material: PVDF: Denka Carbon). All electrolytes were made fresh as and when required. 2032 coin cells were fabricated in a dry room with < -50^{o}C dew point. Electrodes of 0.625" diameter were punched and assembled in a 2032 half-cells and crimped in a Hohsen automatic machine after adding the electrolyte. Cells were evaluated using a series 4000 Maccor tester and impedance was collected using a 1287 Electrochemical Interface/1260 Solatron Impedance Phase Analyzer stack. The electrolyte flammability was evaluated in a home-built apparatus (vide infra) at our thermal abuse facility. Differential scanning calorimetry (DSC) was performed using a TA Instruments Q2000 calorimeter to evaluate the thermal response for the ABA materials and electrolytes. Approximately 10 mg of material was sealed in a high pressure stainless steel DSC pan under inert atmosphere.

Results and Discussion

Conductivity of electrolytes:

Electrolytes consisting of DMMP, 1M TPFB, and xM LiF where x=1, 0.5 and 0.1 were prepared for evaluation and kept under argon until coin cells were fabricated. Figure 2 shows the relationship between temperature and conductivity for electrolytes containing 1M (red), 0.5M (green), and 0.1M (purple) LiF. As expected, the conductivity increases with increasing concentration of LiF. Generally, the difference between conductivity values increases with increasing temperature and decreases with decreasing temperature. The conductivity for the 1M LiF is comparable to that of the conventional battery electrolytes[16]. Figure 3 shows electrochemical voltage window for two electrolytes recorded at a

2 mV/s scan rate. The voltage traces show similar electrochemical characteristics for both DMMP 1M TPFB:1M LiF and DMMP 1M TPFB:0.5M LiF. Both electrolytes show little electrochemical activity throughout the scanned voltage range, indicating stability up to 3.5 V vs. Li/Li^+. The voltage was not scanned beyond 3.5V since this is higher than the cell voltage for this electrochemical couple. However, it has been shown that this type of electrolyte is stable at voltages > 4.2V[9]. The reductive peaks one at ~1.25V and the other at ~2.5V decrease quickly with cycling and were not investigated further. However, likely reasons for these peaks may be associated with the impurities of the pentafluorobenzene boronic acid (98% pure) or the presence of of gaseous species in the electrolytes. Voltage trace for the DMMP 1M TPFB: 0.1M LiF (not shown) are consistent with those reported in Figure 3.

Thermal Studies

DSC measurement

DSC measurement was performed on the ABA salt to evaluate the thermal stability of the material at elevated temperatures. DSC trace in Figure 4 clearly demonstrates that TPFB ABA is stable up to ~340°C. The endotherm at 109°C corresponds to the melting of the compound and the exotherm at high temperature corresponds to the decomposition of the material (similar behavior was observed for other ABAs by us and others)[17,18]. The high temperature stability of the ABA material enhances the overall thermal stability of the DMMP electrolyte, which has consequences for high rate thermal runaway for cells constructed with these materials.

Thermal ramp

At our thermal abuse facility we have a home-built fixture for performing thermal ramp test, shown in Figure 5. This setup consists of a copper block with a pre-drilled hole to accommodate an 18650 cell and two smaller holes for heater cartridges. The line drawing on the right shows the positions of thermocouples in the copper block and the spark source above it. An 18650 cell filled with ~ 5 ml of electrolyte is sealed, crimped, and inserted into the center hole in the copper block as shown on the left. The copper block is heated at a predetermined rate and a spark source positioned above the copper block is turned on to ignite solvent vapor. Flammability test are conducted in this manner for very specific reasons. The positioning of all components in this test (including the electrolyte volume) mimic the worst case scenario for a battery field failure. Several standard flammability tests have been reported and are commonly conducted for battery electrolytes, but they do not necessarily accurately recreate the failure mode of a field failure in which heated cells vent into a potential spark or flame source.

Thermal ramp measurements were conducted on DMMP 1M TPFB:1M LiF electrolytes and a screen capture during the test is shown in Figure 6. While a puddle of electrolyte bubbling on the neck of the cell can't be seen clearly, the figure clearly shows the spark from the spark source above the cell. Any electrolyte vapors that are released from the cell hardware will be directed into the spark source. This test resulted in no ignition or combustion of any material from the cell. The measurement was repeated to ensure reproducible noflammable behavior. After fully characterizing the electrolytes for both thermal and electrical properties, discharge and impedance characteristics were evaluated.

Discharge and Impedance characteristics of CFx cells

Discharge behavior

Figure 7 shows voltage vs. specific capacity traces for 4 different materials evaluated in this study. The performances for B and C comparable and they showed flat voltage profiles for the majority of the discharge. Performance of A is very similar to B and C but exhibits a higher average voltage. Material D starts off at a higher voltage compared to the rest but shows decreasing voltage slope as the discharge progresses. All materials have similar particle size distributions, centered at 10 µm average particle size. Figure 8 shows cell voltage vs. capacity for material C. The initial voltage drop is the highest for the electrolyte containing 0.1M LiF, followed by 0.5M LiF, and the smallest for the 1M LiF, which is the converse of the trend that we see in electrolyte conductivity. The other materials tested exhibited similar trend in voltage. Although the voltage drop is most severe for the 0.1M LiF, as discharge progresses the voltage rises faster than the other LiF concentrations and eventually surpasses the 1M LiF at around 300mAhr/g. The behavior for the 0.5M LiF is similar except that it caught up with the 1M at around 444mAhr/g. The discharge specific capacities for the 1M; 0.5M and 0.1M LiF concentrations are: 727, 751, and 779mAh/g respectively. We believe that the improved performance of the 0.5 and 0.1M LiF can be contributed to the simultaneous decrease in the ohmic and interfacial resistances due to the dissolution of the LiF generated in the discharge reaction by the excess ABA in the solution. In general, of the two factors, the impact of the interfacial resistance on cell performance may be more important than the decrease in the ohmic resistance since the interfacial resistance generally dominates the cell impedance[19,20] and consequently it determines the slope of the discharge curve. For larger interfacial resistances the slope of the curve will also be larger. We mathematically computed the slop ($\Delta V/\Delta T$) from the V vs. time plots (not shown here) for the three discharge curves. Slope is the largest (0.272 V/hr.) for the 1M LiF followed by 0.244 V/hr. for the 0.5M LiF and 0.227 V/hr. for the 0.1M. To verify if the ohmic and interfacial resistances decrease with discharge for the 0.5M and 0.1M LiF we performed impedance measurements at different depth of discharge (DOD) conditions and the data are discussed below.

Impedance Studies

Electrochemical impedance spectroscopy (EIS) was collected at variety of cell voltages (corresponding to different SOCs). Figure 9 shows Nyquist plot of cell impedances for material C1 at different DODs for the DMMP 1M TPFB:1M LiF and DMMP 1M TPFB:0.5M LiF electrolytes. For the 1M LiF, the interfacial impedance increases with DOD and for the 0.5M LiF it decreases with DOD. This observation agrees with our prediction based on the discharge profile of the cell (shown in Figure 8) and this trend is also seen in the DMMP 1M TPFB:0.1M LiF sample (not shown). Figure 10 shows the high frequency impedance data as a function of DOD for the 1M LiF and 0.1M LiF. The ohmic resistance decreases with discharge for 0.1M LiF and remains constant for the 1M LiF. This indicates that the 1M LiF electrolyte does not exhibit ohmic resistance changes during discharge while the 0.1M LiF electrolyte decreases as the cell discharges.

Conclusions

Cells containing sub-stoichiometric amounts of LiF in the electrolyte were demonstrated to perform slightly better than cells containing a 1:1 molar ratio of ABA: LiF by delivering slightly higher capacity. The benefits were shown to correlate to the reduction of both interfacial and ohmic impedance within the cell. Observation of higher capacity and lower interfacial resistance agrees with our prediction that de-fouling the cathode pores of LiF should lead to better performance. Demonstration confirms that the ABA in solution is capable of directly defouling micro porous electrodes, which has implications for not just lithium primary cell chemistry. The ABA was found to be stable up to 340^{o}C and was shown to be nonflammable during thermal flammability testing. These results can be implemented in real world applications by optimizing ABA:LiF ratios to maximize the gains in cell performance.

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