

Short communication

A new chemical approach to improving discharge capacity of $\text{Li}/(\text{CF}_x)_n$ cells

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Abstract

Although $(\text{CF}_x)_n$ has the highest theoretical specific energy of all lithium primary batteries known, the practical specific energy (including packaging) is very small on the order of $\sim 10\%$ for small capacity cells (<5 Ah) and between 20 and 30% for large capacity cells (>100 Ah). Even these can be achieved only at a very low discharge rate $<C/250$ (250 h rate). If either the discharge rate is increased or the discharge temperature is reduced below 0°C the % delivered energy goes down even further. At Sandia National Laboratories we are performing research to improve % delivered energy by: (1) incorporating engineering solution and (2) adopting a new chemical approach. The engineering solution effort will not be discussed here except to mention that light weight metal such as titanium (Ti) will be considered for hardware instead of stainless steel. The chemical approach involves adding an anion-binding-agent (ABA) to the electrolyte solution to dissolve the LiF generated in the discharge reaction. We studied three boron containing neutral ABAs and the most promising ABA {Tris(1,1,1,3,3,3-hexafluoroisopropyl)borate} will be discussed further. The delivered capacity/energy (per unit weight of the cathode) is higher for SNL-built coin cells containing the ABA additive than for the commercial coin cells by 80%. These cells were tested at a $C/44$ rate. This improvement especially at a high discharge rate is attributed to the ability of the ABA to dissolve the LiF from plugging the cathode pores and thus keep the bulk of the cathode accessible for further discharge reaction. We have also tested commercial cells and commercial electrodes in coin cells. In general, at high rate discharge, the performance of SNL cells containing our electrolyte and electrode were better than the rest.

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1. Introduction

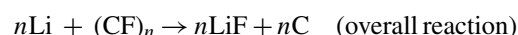
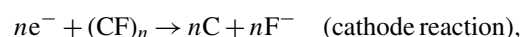
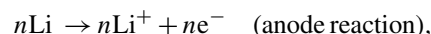
Fluorination of graphite yields a series of compositions denoted by the general formula $\{\text{CF}_x\}_n$ where $x=0.2-1.2$. These are called “graphite fluorides”. Among the many compositions of graphite fluorides three stoichiometric compounds exist. These are $\{\text{CF}\}_n$, $\{\text{C}_2\text{F}\}_n$ and $\{\text{C}_4\text{F}\}_n$. Of the three the most stable is $\{\text{CF}\}_n$ and is traditionally known as “graphite mono fluoride”. This is an excellent lubricant at high temperatures [1] and a good cathode material in primary Li cells with a high theoretical specific energy [2]. Panasonic commercialized this technology in mid 1970s for low rate applications [3]. In Table 1, is compared the theoretical specific energy for different Li-primary cells. Of the four chemistries compared, $(\text{CF}_x)_n$ has a specific energy of 2.2 kWh kg^{-1} . Despite the high-

est theoretical specific energy, the practical energy (this includes cell packaging) is only $\sim 10\%$ of the theoretical (for small cells) while the other cell chemistries exhibit higher practical energy. For large capacity $\text{Li}/(\text{CF}_x)_n$ cells (~ 1000 Ah) however, the delivered capacity is $\sim 30\%$ of the theoretical at very low rates.

At Sandia National Laboratories (SNL) we recognized the high energy of the $(\text{CF}_x)_n$ chemistry and are performing basic research to improve the delivered capacity/energy.

A cursory look at the discharge reaction will tell us where the problem is coming from that leads to poor cathode utilization.

Discharge reaction:



The overall reaction involves generation of carbon and the formation and precipitation of LiF in the cathode pores. LiF is both

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Table 1
Li/(CF_x)_n is compared to other chemistries

Chemistry	Voltage (V)	Specific theoretical (Wh kg ⁻¹) based on active material	Energy practical (Wh kg ⁻¹) for the cell inc. packaging
Li(CF) _n	3.2	2260	220
LiMnO ₂	3.0	1005	200–270
LiSOCl ₂	3.6	1470	320–480
LiSO ₂	3.0	1170	240

an ionic and electronic insulator which might be responsible for the poor cathode utilization. Especially at higher discharge rates the LiF will be precipitated at the mouth of the cathode pores there by limiting access for Li ions to the interior of the cathode for further reaction. This type of behavior has been observed for Li/SOCl₂ cells [4].

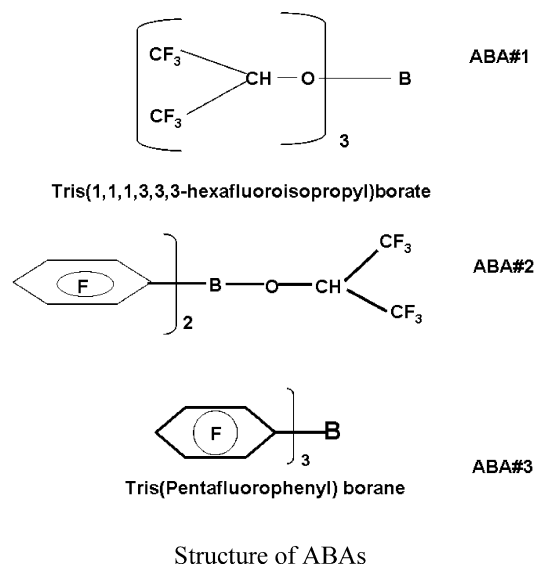
If the presence of LiF in the mouth of the cathode pores is responsible for the poor utilization, then one of the plausible solutions to overcoming this problem will be to dissolve the LiF with an anion binder. Recently, a family of boron-based neutral anion-binding-agents (ABAs) have been prepared [5] and shown to dissolve LiF. At SNL we are pursuing this chemical approach to dissolving LiF. The structures of the ABAs we studied are shown below. The ABA samples were obtained from Brookhaven National Laboratory.

2. Experimental

LiF was purchased from Fisher Scientific, USA. Teflon-60 and PVDF- W#1300 were purchased from DuPont and Kureha, Japan, respectively. (CF_x)_n was purchased from Advance Research Chemicals (Catoosa, Oklahoma, USA). Gulf Shewingin Acetylene black was used as conductive additive to the cathode. All these chemicals were baked out at 100 °C overnight before using. Battery grade solvents ethylene carbonate (EC), dimethyl carbonate (DMC) were purchased from Mitsubishi chemicals and were used as received. 18,650 and coin cell hardware were purchased from Hohsen, Japan. Celgard 2325 was purchased from Celgard, Charlotte, North Carolina, USA was used as separator. Mainly we used two electrolytes in our studies that are described below. We studied electrolyte with LiF and ABA#1 dissolved in EC-DMC. Molecular weight for the three ABAs is around 511 and these dissolve in EC-DMC mixed electrolyte easily. Of the three ABAs, ABA#1 is reported to have the highest conductivity in EC-DMC (1:2%, v) containing 1 M LiF [5]. Because of the higher conductivity we used ABA#1 in our studies. Our electrolyte have EC:DMC (1:2%, v) as mixed solvent, 0.8 M LiF as salt and 1.2 M ABA#1 as anion binding agent. This electrolyte is denoted as SNL-ABA1.

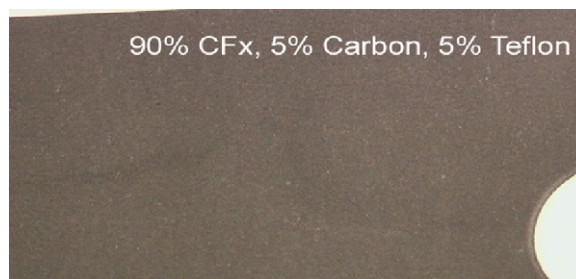
We also used EC-EMC (3:7%, w)/1.2 M LiPF₆ electrolyte in our initial evaluation of cathode material. This electrolyte is denoted as high conductivity electrolyte (HCE). In addition, we studied commercial electrolytes. The three electrolytes are described below.

- (1) EC-DMC (1:2%, v) containing 0.8 M LiF and 1.2 M ABA#1 is denoted SNL-ABA1.
- (2) EC-EMC (3:7%, w) containing 1.2 M LiPF₆ is denoted as HCE (high conductivity electrolyte).
- (3) Commercial electrolyte.



2.1. Electrode and cell fabrication

We made several batches of (CF_x)_n electrodes with Teflon as a binder. For initial evaluation of electrodes to check for uniformity of loading we used coin cells (2016 configuration). The procedure for making electrode is described below. Teflon (5%, w), conductive carbon (5%, w) and (CF_x)_n (90%, w) were dry blended and a small (~2 ml) of high purity water was added and the mixture was kneaded to a dough like consistency (adding water as and when required during the kneading process). This material was rolled by hand with an aluminum rolling pin, on a stainless sheet. After rolling and folding and rolling more several times the desired thickness was achieved. The electrode was dried overnight in a dry-room before calendaring to achieve uniform thickness across the electrode. A photograph of the electrode is given below. Several electrode samples were punched out from across the electrode to check for uniformity of thickness and mass loading. We used Hohsen CR 2016 cell crimper for making coin cells.



Photograph of Sandia made electrode with Teflon as binder. Electrode composition is given in the picture itself.

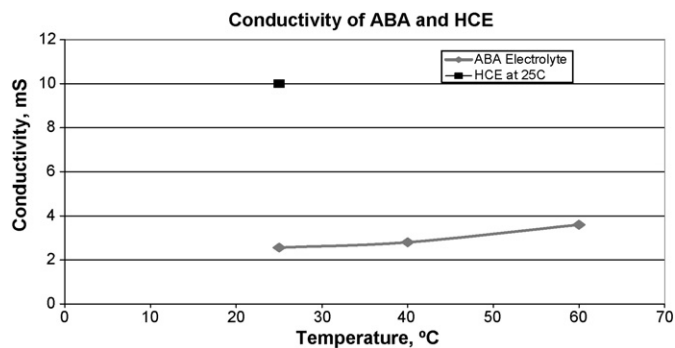


Fig. 1. Ionic conductivity vs. temperature for SNL-ABA along with that for HCE.

3. Results and discussion

3.1. Conductivity measurement

Our conductivity values for SNL-ABA1 (shown in Fig. 1 at three different temperatures) are comparable to the literature value [5]. Also the conductivity value for the HCE is given in the figure for comparison.

The conductivity at 25 °C for the SNL-ABA1 is ~ 4 times lower than for the HCE. For example at 25 °C the conductivity for HCE is around 10 mS cm^{-1} and for the SNL-ABA1 is around 2.5 mS cm^{-1} .

3.2. Coin cell studies

We studied two different electrodes (SNL and commercial) and two types of cells (SNL and commercial). The electrochemical data collected at SNL on these are discussed below.

3.2.1. Discharge behavior of SNL prepared electrodes

We made several coin cells typically 2016 size (2 cm diameter and 0.16 cm thick) for testing and evaluation of the electrodes. These electrodes were made at SNL. The main purpose for evaluating several coin cells is not only to assess the loading of active material across the length of the electrode but also to check for batch to batch reproducibility.

In Fig. 2 are shown typical discharge curves for coin cells containing ABA1 and HCE electrolytes. Although the cell with ABA has a higher initial voltage drop, it performed ~ 5 h longer

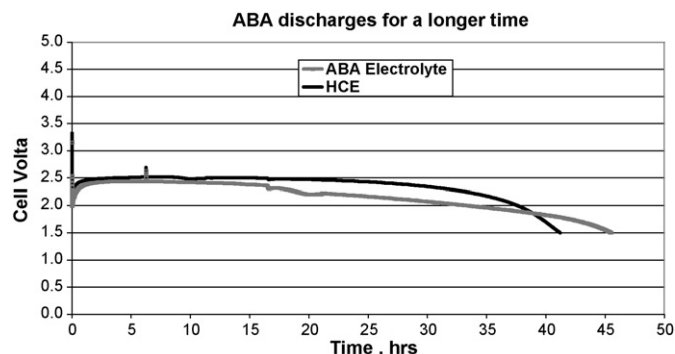


Fig. 2. Cell voltage vs. time for SNL-built coin cell at 25 °C.

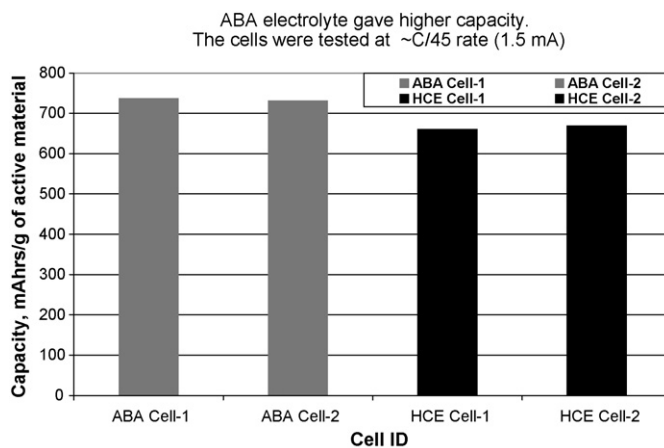


Fig. 3. Specific capacities for cathode material are plotted for the two electrolytes.

than the other cell. The cells were discharged at a 1.5 mA constant current.

The capacity values calculated from Fig. 2 are converted into specific capacity per gram of active material and plotted in Fig. 3. In Fig. 3 is compared specific capacity per gram of active material for two cells each of the two electrolytes. In Fig. 3, ABA-1 denotes cell 1 with SNL-ABA1 electrolyte. HCE-1 denotes cell 1 with HCE electrolyte. The specific capacity is lower for the HCE containing cell. Fig. 3 clearly shows that ABA containing cells gave ~ 70 mAh higher specific capacity per gram of active material than the HCE containing cell.

This observation is contrary to the expectation since HCE has a higher conductivity than SNL-ABA1. This observation probably suggests that while a high ionic conductivity in the electrolyte is necessary it is not sufficient to improve performance. Perhaps the interfacial resistance may be important and critical to improving cell performance. This aspect is discussed later.

3.2.2. Performance comparison of SNL and commercial cells

The SNL cells contain SNL-ABA1 electrolyte. In addition to testing SNL built cells we also tested commercial coin cells (typically 2016 type) at the same discharge current for comparing specific capacity. In Fig. 4 are compared the specific capac-

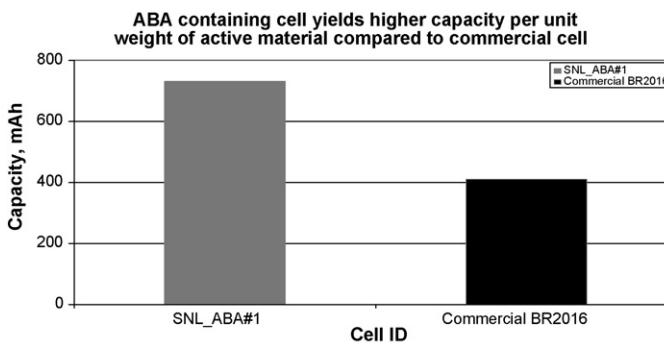


Fig. 4. Comparison of SNL-built and commercial cells for specific capacity per gram of active material.

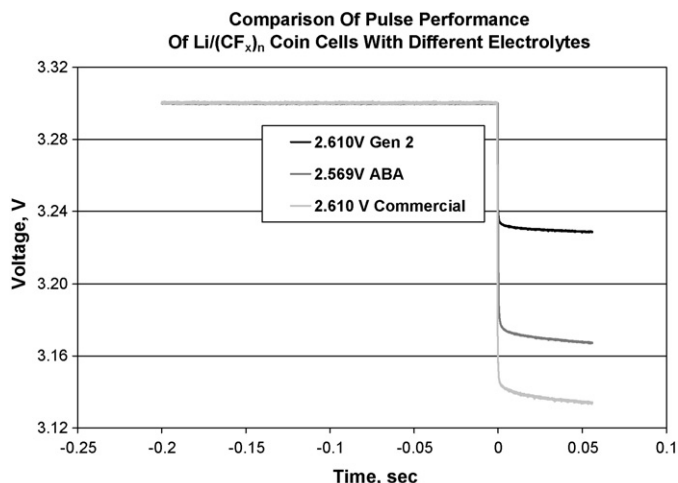


Fig. 5. Voltage response of cells for a 2.8 mA discharge pulse.

ity per unit weight of the cathode material for SNL-ABA1 and commercial 2016 cell. The cells were tested at 25 °C and 1.5 mA current which corresponds to a C/44 rate. SNL cells gave ~80% higher capacity than the commercial cells for unit weight of the active material. The commercial cells are designed for low rate discharge. However, our tests were done at a higher rate. This explains why the commercial cells did not perform well at higher discharge rates.

3.2.3. Performance of cells made with commercial electrodes in different electrolytes

We also made coin cells with commercial electrodes and tested them in the three electrolytes. In Fig. 5 are shown voltage responses for the three cells for a 2.8 mA discharge pulse. The initial voltage drops for the three cells are: HCE = 70 mV; ABA1 = 130 mV and commercial = 170 mV. This trend reflects the trend in conductivity of the electrolytes. The cell with the HCE electrolyte showed the lowest voltage drop followed by SNL electrolyte and the highest voltage drop was observed for the commercial electrolyte. This data suggest that if the cells are discharged at the same discharge current the delivered capacity should decrease in the order given below: HCE > ABA > commercial electrolyte. In Fig. 6 are compared the specific capacity per unit weight of cathode in the three electrolytes.

The cells were discharged at a 600 μA current. Contrary to expectation the cell with ABA1 electrolyte out performed the HCE by ~40 mAh g⁻¹ of cathode. Again this underscores the importance of the interfacial resistance.

3.2.4. Role of interfacial resistance in cell reaction

We have shown above that the performance of the HCE is inferior to that of the SNL-ABA1. To see if the interfacial resistance is lower for cells containing SNL-ABA1 electrolyte than the HCE or the commercial electrolyte, we performed impedance studies on coin cells containing these electrolytes. In Figs. 7–9 are shown respectively Nyquist plots of impedance for the SNL built coin cells containing SNL-ABA1 electrolyte, HCE and commercial electrolyte. The plots clearly show that the interfacial impedance for the ABA electrolyte is the smallest

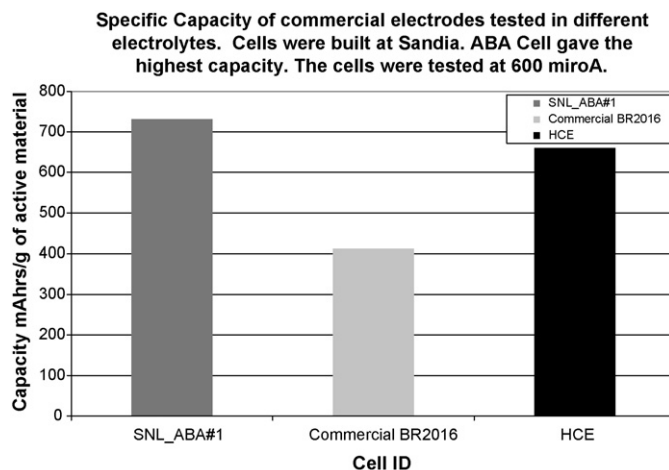


Fig. 6. Specific capacity per gram of active cathode material for commercial electrode in the three electrolytes.

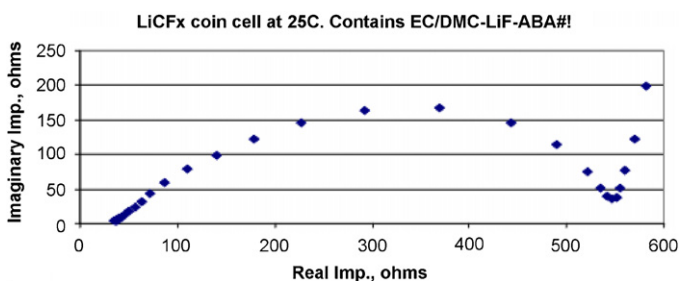


Fig. 7. Nyquist plot of impedance for the SNL-ABA containing coin cell.

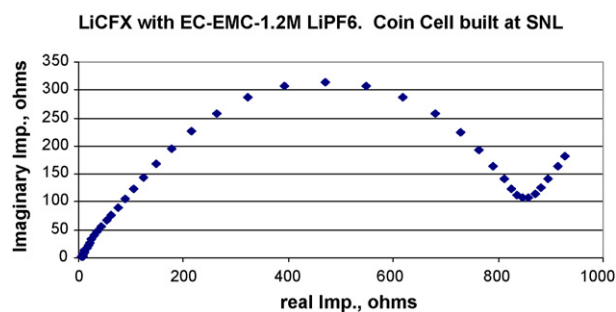


Fig. 8. Nyquist plot of impedance for HCE containing coin cell.

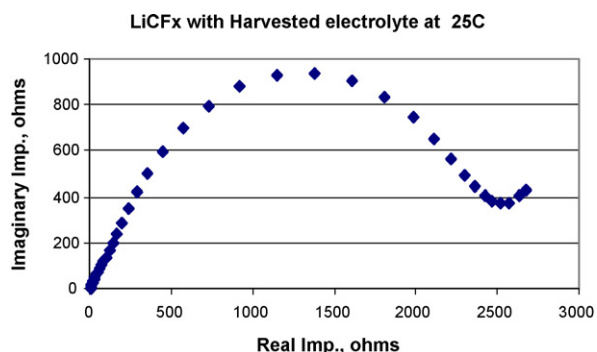


Fig. 9. Nyquist plot of impedance for commercial electrolyte containing coin cell.

of the three followed by the HCE and the commercial electrolyte. The interfacial resistance decreases in the following order: commercial electrolyte > HCE > ABA1. This observation clearly underscores the importance of the interfacial resistance in the overall performance of the cell. We believe that the deposition of LiF on the surface of the cathode and in the mouth of the electrode pores can cause the interfacial resistance to increase. This situation may happen at high discharge rates as in this case where cells were discharged at a C/44 rate which is a high rate for Li/(CF_x)_n cells. The ability of the ABA to dissolve the LiF leads to lowering of the interfacial resistance. We have no data to show that the presence of ABA in the electrolyte lowers the build-up of the LiF on the electrode surface. However, if free ABA is present in the solution (in our case it is true since our electrolyte has more ABA by 0.4 M over the LiF concentration) the LiF formed in the discharge reaction should go into solution. However, it should be mentioned here that the concentration of excess ABA will not be sufficient to dissolve all of the LiF formed in the discharge reaction. Others have reported similar observations where the electrolyte with lower conductivity showed superior performance because of much lower interfacial resistance [6].

4. Conclusion

Recently we have initiated at Sandia a program to improve performance of Li/(CF_x)_n cells. We made several batches of

(CF_x)_n electrodes with Teflon as the binder. These electrodes were tested in coin cells in three different electrolytes. These cells containing Sandia electrode and electrolyte gave the best performance in terms of the delivered capacity per gram of the active cathode material. Although the HCE has the highest conductivity its performance is inferior to that of SNL-ABA1 electrolyte. This trend was observed with commercial electrodes as well.

Acknowledgements

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