

Short communication

# Performance enhancement at low temperatures and in situ X-ray analyses of discharge reaction of $\text{Li}/(\text{CF}_x)_n$ cells

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Received 8 March 2007; received in revised form 2 April 2007; accepted 3 April 2007

Available online 18 April 2007

## Abstract

In the Sandia National Laboratories internally funded Laboratory Directed Research and Development (LDRD) project we are studying the fundamental limitation(s) of the discharge reaction that reduces the operating voltage of the  $\text{Li}/(\text{CF}_x)_n$  cells at moderate discharge rates. As a subset of this effort, we are evaluating the electrochemical properties of  $(\text{CF}_x)_n$  electrodes prepared with materials from different vendors at different temperatures and in two different electrolytes in order to provide an optimized system to the above study. The temperatures studied span the range  $-51$  to  $72^\circ\text{C}$ . The electrolytes consist of EC:EMC (3:7 wt.%)–1.2 M  $\text{LiPF}_6$  denoted as HCE (Highly Conductive Electrolyte) and EC:PC:EMC (1:1:3 wt.%)–1 M  $\text{LiBF}_4$  denoted as SNL-E (Sandia National Laboratories Electrolyte). The four different  $(\text{CF}_x)_n$  materials studied showed comparable capacity at  $0^\circ\text{C}$  and above in the two electrolytes. However, at sub-ambient temperatures the SNL-E performed better than the HCE. The performance improvement with SNL-E comes mainly from a lower interfacial resistance compared to HCE.

The different  $(\text{CF}_x)_n$  materials performed differently in the SNL-E especially at sub-zero temperatures. For example, at sub-zero temperatures the delivered capacity varied between 6% and >60% of the room temperature capacity. In order to rationalize this observation, SEM photographs of the powder particles were taken that showed that the particle size of the best performer(s) is smaller than that of the others. Finally, these data seem to indicate that optimization of the properties of the electrolyte as well as the electrode is critical to maximizing delivered capacity especially at sub-ambient temperatures.

Our X-ray results shall be presented in more detail in an upcoming manuscript. We have elected to present a brief discussion of these results in this present paper as the findings lend support to the formation of intermediate species in the discharge reaction of  $\text{Li}/(\text{CF}_x)_n$  cell.

Published by Elsevier B.V.

**Keywords:** Carbon monofluoride; Impedance; PVDF; Interfacial resistance

## 1. Introduction

Lately there is growing interest in improving the performance of  $\text{Li}/(\text{CF}_x)_n$  cells for space and military applications. Of all the known ambient temperature Li-primary chemistries  $\text{Li}/(\text{CF}_x)_n$  has the highest theoretical specific capacity and energy (vide infra Table 1). The theoretical specific energy and capacity are for  $x = 1$  (each carbon has one F attached). However, the practical energy is only 10–35% of the theoretical depending on the discharge rate and cell size. One of the reasons for the poor performance may be coming from low operating cell voltage ( $\sim 2.5$  V) which is much lower than the OCV of  $\sim 3.4$  V. In

general, there seems to be a consensus in the scientific community that an intermediate species (in the discharge reaction) is responsible for the depression in the operating voltage. During the 1970s and 1980s several researchers proposed reaction schemes but without irrefutable proof for their hypotheses. For example, Hagiwara et al. [1] based on their analyses of discharge products and OCV measurements in different solvents proposed that the discharge reaction includes electrochemical formation of an intermediate phase comprising of  $\text{Li}^+$ , (CF) and solvent molecule and the subsequent chemical decomposition of the intermediate to the final products. However, there was no proof for the existence of the intermediate species. Whittingham et al. [2] proposed that a ternary non-stoichiometric intercalation compound of the type  $(\text{CLi}_x\text{F})_{x < 1}$  formed in the discharge reaction determined the OCV of the cell. He also suggested that when  $(\text{CF}_x)$  is chemically reduced its inter-planer spacing

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Table 1  
Comparison of the electrochemical properties of Li primary cells

Chemistry	Voltage (v)	Specific energy (Wh kg <sup>-1</sup> )		% theoretical
		Theoretical	Practical	
Li/MnO <sub>2</sub>	3.0	1005	200–270	
Li/SO <sub>2</sub>	3.0	1170	240	
Li/SOCl <sub>2</sub>	3.6	1470	430	~30
Li(CF <sub>x</sub> ) <sub>n</sub>	3.2	2260	220	~10

expands to 9.35 Å. However, this type of lattice expansion could not be confirmed in an electrochemically reduced material.

At Sandia National Laboratories we are working on an LDRD program aimed at understanding the discharge reaction mechanism to propose solution(s) for increasing the operating voltage close to 3.0 V at moderate discharge rates. In the LDRD effort we will be using techniques such as TOFSIMS (Time of Flight Secondary Ion Mass Spectroscopy), STM (Scanning Tunneling Microscopy), etc., to look at directly the discharge mechanism. This work will be published elsewhere. As a subset of this effort we are looking at (CF<sub>x</sub>)<sub>n</sub> materials from different sources to select the best material (for capacity) for the above study. In this paper we describe the electrochemical data on Sandia-built Li/(CF<sub>x</sub>)<sub>n</sub> coin cells and compare performance especially at low temperatures in two different electrolytes.

We have developed a method for in situ XRD analysis of “pouch” cells for the purposes of obtaining information on the structure/property relationships regarding battery systems [3,4]. In the pouch technique, a functional cell (cathode, separator, anode, electrolyte, etc.) is assembled within a very thin plastic baggie, and then vacuum-sealed in such a way as to allow the electrode leads to exit the sealed pouch. Sufficient penetration of X-rays through the low-Z materials that make up the pouch cell allows scrutiny of structural changes occurring within the anode and/or cathode as the functional cell is discharged. We employed this technique to analyze the (CF<sub>x</sub>)<sub>n</sub> cathode material as a function of discharge.

## 2. Experimental

Four different (CF<sub>x</sub>)<sub>n</sub> cathode materials were purchased from three vendors. The different materials are denoted as (CF<sub>x</sub>)<sub>n</sub>-1; (CF<sub>x</sub>)<sub>n</sub>-2; (CF<sub>x</sub>)<sub>n</sub>-3; (CF<sub>x</sub>)<sub>n</sub>-4. (CF<sub>x</sub>)<sub>n</sub>-3 and (CF<sub>x</sub>)<sub>n</sub>-4 were purchased from the same vendor. These materials differ in % fluorine content and in particle size (see below SEM photographs). The value of *x* in these materials is

$$(CF_x)_n-1; x =: 0.8 - 1.2; \quad (CF_x)_n-2; x =: 1.02;$$

$$(CF_x)_n-3; x =: 1.0 \quad \text{and} \quad (CF_x)_n-4; x =: 0.9 - 1.0$$

The average particle size of (CF<sub>x</sub>)<sub>n</sub>-1 is ~8 μm, that of (CF<sub>x</sub>)<sub>n</sub>-2 is around 5–6 μm and that of (CF<sub>x</sub>)<sub>n</sub>-3 and (CF<sub>x</sub>)<sub>n</sub>-4 is around 4 μm. Kureha PVDF was used as binder along with carbon (Gulf Shawinigan Acetylene Black) for improving the electronic conductivity of the electrode. These materials were vacuum baked at 100 °C overnight before using. The battery

grade solvents ethylene carbonate (EC); propylene carbonate (PC); ethyl methyl carbonate (EMC) purchased from Mitsubishi Chemicals (Japan) were used as received. The lithium salts (LiPF<sub>6</sub> and LiBF<sub>4</sub>) purchased from Hashimoto, were vacuum dried at 60 °C overnight before using.

### 2.1. Electrode making

PVDF is dissolved in NMP followed by the addition of carbon. This mixture is stirred to disperse carbon uniformly before adding the (CF<sub>x</sub>)<sub>n</sub> powder. This mixture is stirred for an hour before making electrodes. This mixture is a slurry with an aggregate particle size of ~3–5 μm and with a typical composition of 5 wt.% each of the PVDF and carbon and 90 wt.% (CF<sub>x</sub>)<sub>n</sub>. This is coated on to a carbon coated (3 μm thick) aluminum current collector (~12 μm thick) in a Hohsen coater model # HSCS-200. The typical thickness of the dried electrode is ~72 μm. In a typical coating run several meters-long electrodes were prepared. The electrodes are baked in vacuum at 100 °C overnight before testing them in coin cells.

Electrodes (~2 cm<sup>2</sup> area) for the coin cells (2032 size; 2 cm diameter and 0.032 cm thick) were punched from these large electrodes.

Two different electrolytes were used in our study. The compositions of the electrolytes are given below—Highly Conductive Electrolyte (HCE): EC:EMC (3:7 wt.%)–1.2 M LiPF<sub>6</sub>; Sandia Electrolyte (SNL-E): EC:PC:EMC (1:1:3 wt.%)–1 M LiBF<sub>4</sub>.

The ionic conductivity of HCE is ~10 mS cm<sup>-1</sup> around room temperature and that of SNL-E is ~4–5 mS cm<sup>-1</sup>. HCE exhibited higher ionic conductivity at all temperatures investigated in this study. Several coin cells with Sandia-coated electrodes were prepared containing these electrolytes. A suite of electrochemical measurements including impedance and discharge at different temperatures were performed to characterize cell behavior.

### 2.2. Impedance measurement

Impedance measurements were carried out in three-electrode configuration in T-Cells at a couple of different temperatures. The three-electrode configuration allows the measurement of the full cell, cathode and anode impedances. The Solatron impedance equipment consisting of SI 1287 Electrochemical Interface and 1255B Frequency Response Analyzer controlled with Zplot was used for impedance studies. The cell impedance was measured between 100 kHz and 100 mHz. A minimum of two cells were studied for each-chemistry and the cell-average was plotted in Figs. 6 and 7.

## 3. Results and discussion

### 3.1. Discharge studies

SNL-built coin cells were used for the studies. The cells were discharged in a Maccor tester model # Series 4000. A typical discharge curve for one of the (CF<sub>x</sub>)<sub>n</sub>-3 cells is given in Fig. 1. The cell was discharged at a C/200 rate and 25 °C. The voltage

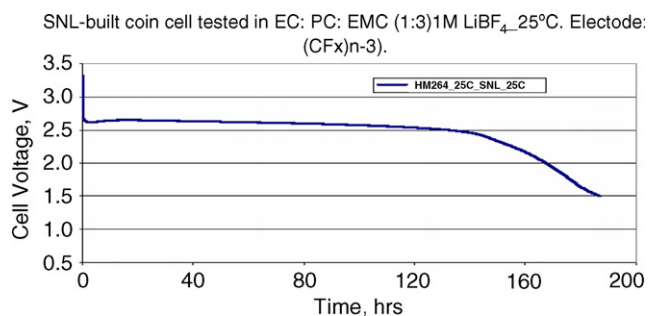


Fig. 1. Voltage response of a Sandia-built coin cell for a C/200 discharge rate at 25 °C.

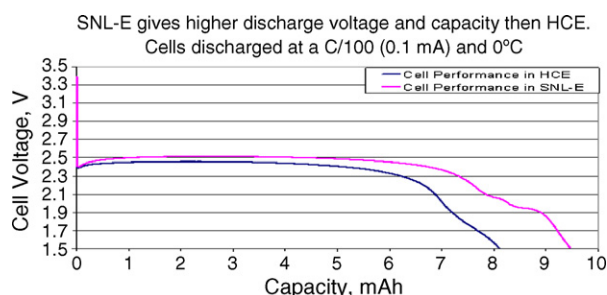


Fig. 2. Cell voltage vs. delivered capacity at a C/100 rate (0.1 mA) and 0 °C.

dropped initially and remained nearly flat for all most 100 h before starting to decrease. Similar behavior was observed for the other materials.

Even at a C/200 rate the operating voltage is only around 2.6 V which is about 0.6–0.8 V lower than the OCV. The measured capacity of the cell is  $\sim 9$  mAh which is 99% of the theoretical capacity based on the weight of the cathode active material in the cell. Similar tests were performed at different temperatures for the four different  $(CF_x)_n$  materials.

In Figs. 2 and 3 are compared the discharge curves for the two electrolytes at two rates and 0 °C. At C/100 and C/5 rates the SNL-E gave higher operating voltage and capacity than the HCE. At C/5 the improvement in performance with SNL-E is higher than at C/100.

In Fig. 4 are compared the discharge capacity for the  $(CF_x)_n-1$  in the two electrolytes at different discharge rates.

The solid curves are for the HCE containing cells and the dashed lines are for the SNL-E containing cells. The delivered capacities at C/5; C/50; C/100 and C/200 rates and at tempera-

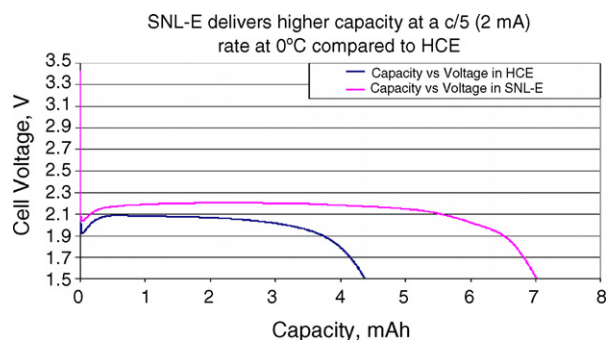


Fig. 3. Cell voltage vs. delivered capacity at a C/5 rate (2 mA) and 0 °C.

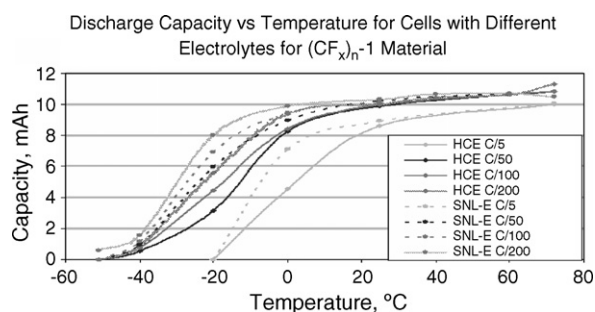


Fig. 4. Discharge capacity vs. temperature for the  $(CF_x)_n-1$  material in the two electrolytes.

tures in the range  $-51$  to  $72$  °C are compared. The plots clearly show that the performance of SNL-E containing cells in general is better than the HCE containing cells especially at sub-ambient temperatures. In general, this behavior is true for the other  $(CF_x)_n$  materials investigated in this study. For example, the behavior of  $(CF_x)_n-2$  is similar to  $(CF_x)_n-1$  as shown in Fig. 5. The other two materials also showed improved performance in SNL-E. However, we tested them only at a couple of temperatures.

Although HCE has higher ionic conductivity than the SNL-E the electrochemical performance of the SNL-E is superior. Obviously the trend in the ionic conductivity cannot explain this observation. The observed performance can be explained by the interfacial resistance. This is explained in the next section.

### 3.2. Effect of interfacial resistance on performance

In Figs. 6 and 7 are shown Nyquist plots of impedance at 25 °C and  $-20$  °C respectively for the cathode at the same cathode voltage (2.9 V) in the two electrolytes. For each cell, at temperature, the full-cell, cathode and anode impedances were measured. Over 90% of the full-cell impedance comes from the cathode. Since the cathode contributes to majority of cell impedance, only the cathode impedances are compared. These plots indicate clearly that the interfacial resistance of cathode in SNL-E is lower than the HCE. However, the cell with SNL-E shows higher ohmic (high-frequency) resistance than the HCE electrolyte. In Fig. 6B are shown expanded view of the Nyquist plots. There are two arcs at the higher frequencies seen for SNL-E. However, the arcs are convoluted for the HCE. Others have seen two arcs for  $LiCoO_2$  cathode [5]. Since it is not the intent

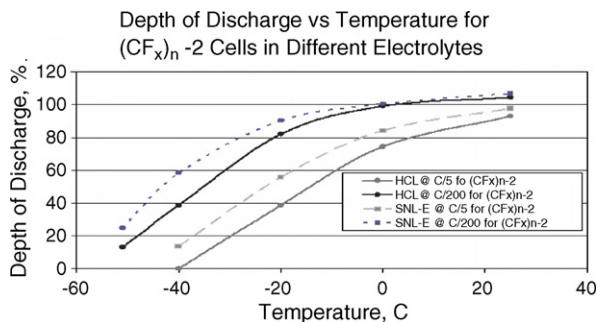


Fig. 5. % discharge capacity vs. temperature for the  $(CF_x)_n-2$  material in the two electrolytes.

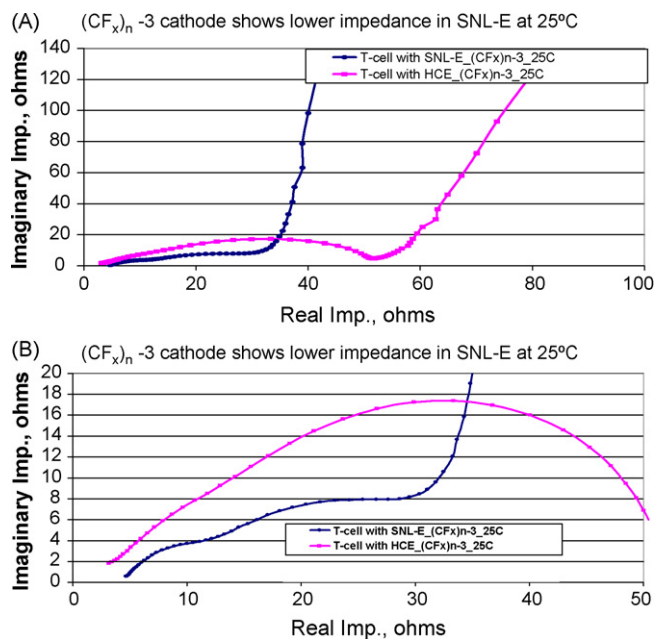


Fig. 6. (A) Nyquist plot of impedance for  $(CF_x)_n$ -3 at 25 °C in the two electrolytes. (B) Expanded view of Nyquist plot of impedance for  $(CF_x)_n$ -3 at 25 °C in the two electrolytes.

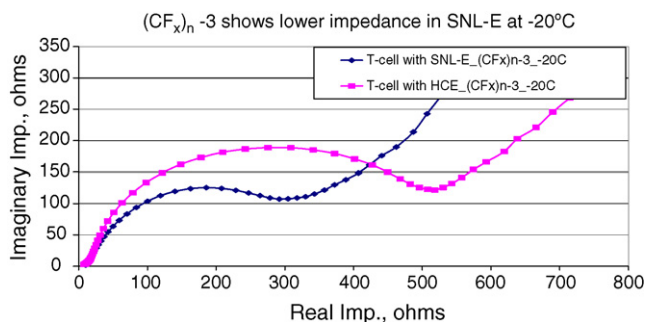


Fig. 7. Nyquist plot of impedance for  $(CF_x)_n$ -3 at -20 °C in the two electrolytes.

of this paper to critically analyze the impedance data, but to show that electrolytes with lower cathode/electrolyte interfacial resistance performs better, the readers are referred to Ref. [5] for analyses for a similar data. At -20 °C the difference in interfacial resistance is much more dramatic than at 25 °C which implies that HCE should perform progressively worse at sub-ambient temperatures than the SNL-E. This observation clearly suggests that it is not sufficient to increase the ionic conductivity of the electrolyte but improve the electrode/electrolyte interfacial resistance. Similar observation has been reported by

Table 2  
Impedance values for the coin cells with the two electrolytes

Temperature (°C)	HCE			SNL-E		
	Ohmic (Ω)	Total (Ω)	(Total-ohmic) <sup>a</sup>	Ohmic (Ω)	Total (Ω)	(Total-ohmic) <sup>a</sup>
25	3	79	76	5	41	36
-20	7	746	739	10	526	516

<sup>a</sup> Ohmic resistance subtracted from the total resistance. The total and the ohmic resistances are taken at 100 mHz and 100 kHz, respectively, corresponding to the lowest and the highest frequencies cell impedance was measured at.

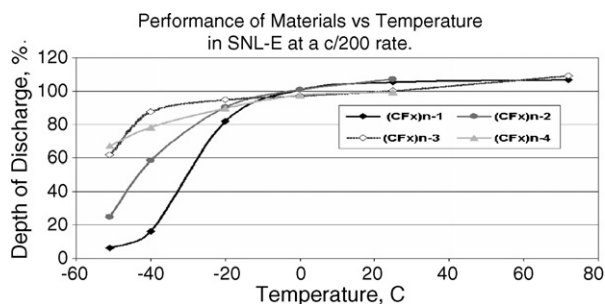


Fig. 8. Performance of the  $(CF_x)_n$  materials in SNL-E at different temperatures at a C/200 rate.

Table 3  
% discharge capacity at different sub-ambient temperatures

Temperature (°C)	$(CF_x)_n$ -1	$(CF_x)_n$ -2	$(CF_x)_n$ -3	$(CF_x)_n$ -4
-20	82	82	95	90
-40	16	39	88	82
-51	6	25	62	67

Tested in SNL-E and at a C/200 rate.

others for Li-ion cells [6]. In Table 2 are given the ohmic and the total cell resistances culled from the impedance plots for cells containing the two electrolytes. At both temperatures the cathode showed lower cell impedance in the SNL-E compared to HCE. We also performed three-electrode impedance measurements on the  $(CF_x)_n$ -1 and  $(CF_x)_n$ -2 cathodes and observed similar electrolyte behavior.

Based on the above observation we continued our investigation on the other materials mainly in SNL-E. In Fig. 8 are compared the discharge capacities for the four different materials in SNL-E at different temperatures. In Table 3 the performance values culled from Fig. 8 are given.

The performance at a C/200 rate of the different materials is comparable above 0 °C. However, the performance at sub-zero temperatures varies significantly. For example, at sub-ambient temperatures the performance of  $(CF_x)_n$ -3 is better than the rest (except at -51 °C). At -40 °C, while  $(CF_x)_n$ -3 gave ~88% of the capacity  $(CF_x)_n$ -1 gave only 16%. At -51 °C the performance of  $(CF_x)_n$ -3 is very nearly comparable or slightly lower to that of the  $(CF_x)_n$ -4.

In this study we used the SNL-E which showed best electrochemical properties. However, the discharge capacity was different for the different materials. Probably the difference has come from the particle size of the material. We took SEM photos of the  $(CF_x)_n$  powders to see if they have different particle sizes. The SEM photos for the four materials are shown below.



The photos of the four  $(CF_x)_n$  powders show that the powder particles have different particle sizes. For example, at  $20\ \mu\text{m}$  magnification the particle size decreases in the following order:

$(CF_x)_{n-1} > (CF_x)_{n-2} > (CF_x)_{n-3} \sim (CF_x)_{n-4}$ . Materials with smaller particle size perform better. Finally, this observation also emphasizes that both the electrode and the electrolyte properties should be optimized to maximize cell performance.

### 3.3. X-ray studies

Fig. 9A and B shows a summary plot of both the voltage curve obtained during discharge of our pouch cell, along with a contour plot of the XRD data collected using a Siemens D500  $\theta$ – $\theta$  diffractometer ( $\text{Cu K}\alpha$ ,  $\lambda = 1.5406\ \text{\AA}$ ).

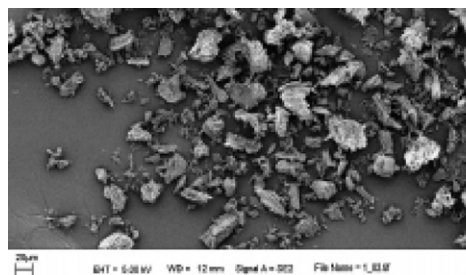


Photo of  $(CF_x)$ -1

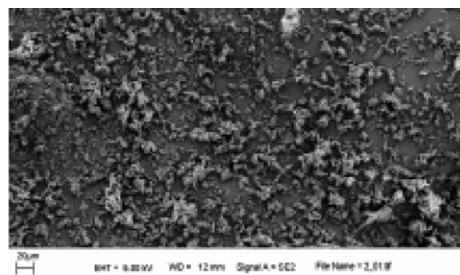


Photo of  $(CF_x)$ -2

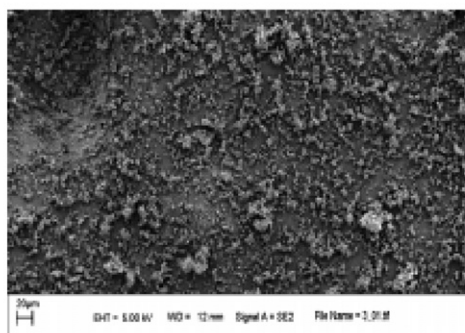


Photo of  $(CF_x)$ -3

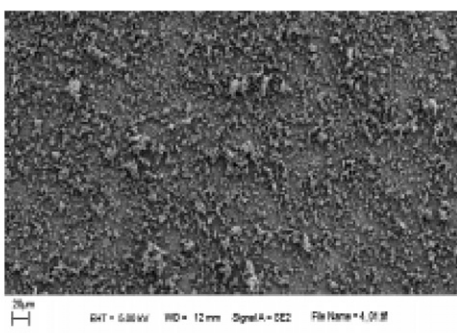


Photo of  $(CF_x)$ -4

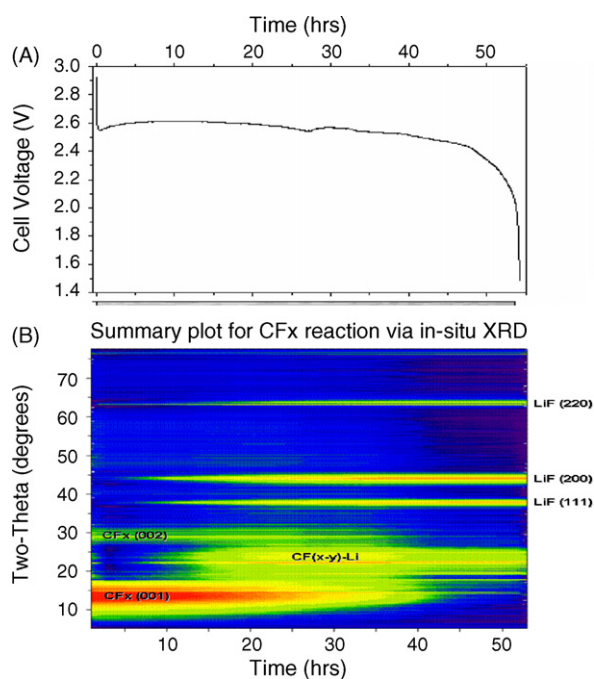


Fig. 9. (A) Discharge curve for our pouch cell, along with a contour plot of the XRD data collected during discharge. (B) A contour plot of the XRD data collected during discharge.

The voltage curve shows typical discharge behavior for  $(CF_x)_n$ , with a precipitous drop from OCV at the onset of the discharge process, to a plateau voltage of  $\sim 2.6\ \text{V}$ . This plateau voltage persists until the onset of cell failure. The XRD analysis is shown below the voltage curve as a contour plot, having axes of  $x = \text{time}$ , and  $y = 2\theta$  angle and the intensity (as a log scale) shown as a color scale. The contour plot shows significant presence of the  $(CF_x)_n$  cathode material at the beginning of cell discharge as illustrated by the prominent  $(CF_x)_n$  (001) intensity at  $\sim 10^\circ 2\theta$ . The contour plot shows the  $(CF_x)_n$  intensity dissipating as the cell progresses through discharge. LiF peaks are observed to mature concurrent with the decay of the  $(CF_x)_n$  intensity. These observations are consistent with other published results [7–9]. A thorough analysis of the XRD data using multivariate analysis (MVA) cleanly separated the  $(CF_x)_n$  feature from scattered intensity due to the fixed components of the pouch cell (e.g. separator). Moreover, the MVA technique suggested that another species, perhaps an intermediate phase, formed during cell discharge as well shown in the contour map as  $\text{CF}_{(x-y)}\text{-Li}$ . An in-depth discussion regarding these observations, along with further detail regarding MVA of the obtained XRD dataset is in preparation and shall be presented soon.

#### 4. Conclusions

We tested four different  $(CF_x)_n$  materials in two different electrolytes namely HCE and SNL-E. Although HCE showed higher ionic conductivity, its performance was inferior to that of the SNL-E especially at sub-ambient temperatures. Our impedance data showed that SNL-E exhibited lower interfacial resistance than the HCE electrolyte. This observation highlights the importance of lowering interfacial resistance to improving performance. Among the four different materials investigated,  $(CF_x)_n-4$  which has the smallest particle showed improved performance. Our work highlights the importance of improving both the electrode and electrolyte properties for increasing performance.

We performed in situ X-ray on pouch cells during discharge and the X-ray data was analyzed using MVA. The MVA analysis strongly suggests the formation of an intermediate species.

#### Acknowledgments

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. The authors would

like to thank the Laboratory Directed Research and Development (LDRD) program for funding this work. The authors would also like to thank Lorie Davis for preparing and testing cells.

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