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Microcalorimetry of Li/CF_x Cells and Discharge Mechanism

**by Jeffrey Read, Donald Foster, Jeffrey Wolfenstine,
and Sheng Zhang**

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Sensors and Electron Devices Directorate, ARL

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14. ABSTRACT The Li-CF _x chemistry has been traditionally used for low rate applications at discharge rates of C/1000 or lower. The Army is supporting efforts to engineer Li/CF _x batteries for Soldier applications that operate at higher rates, closer to C/10. This effort is based on the favorable specific energy and storage characteristics offered by this chemistry. Heat generation under high rate discharge is one potential concern in these batteries and, therefore, further study of the mechanism of heat generation and the differences in heat generation between various CF _x materials is warranted. We demonstrate that the thermal power generated when a Li-CF _x cell is discharged appears nearly instantaneously in the cell and ceases nearly as quickly when discharge is interrupted. Extrapolation of the running potential to zero heat results in a predicted voltage for the Li/CF _x cell of 4.25 V, very near the theoretical potential calculated by Wood, et al. (1). The microcalorimetry results support the two phase model for discharge where a large overpotential, presumably due to the highly disfavored process of breaking covalent C-F bonds, dominates the OCV and running potential of the cell.					
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1. Introduction

Li-CF_x batteries are proposed for use in Soldier applications where a high specific energy primary power source is needed. Li-CF_x D-cells have demonstrated the rate capability necessary for Soldier applications (2, 3, 4, 5). One problem that needs to be addressed is the heat generated on discharge, which can be significant at higher discharge rates (3, 4). Microcalorimetry on Li-CF_x cells (6) has been carried out, but a more detailed examination is warranted.



The overall discharge reaction of a Li-CF_x cell is shown in equation 1. The E^o value is given by Wood et. al. (1). for a CF_{1.0} material. The open circuit voltage (OCV) of a Li-CF_x cell is normally 3.1–3.6 V, significantly lower than the theoretical value above. This difference between theoretical potential and the observed OCV has been ascribed to the formation of ternary phases (7, 8) such as CLi_xF or CFLi_x:S_y where S is a solvent molecule that is co-intercalated with a lithium ion. It is proposed that the kinetics for formation of an intercalated phase is more favorable than the kinetics of the direct two phase reaction. It is also proposed that the resulting intercalated phase decomposes over time to produce the final products carbon and LiF. The significant amount of heat generated by a Li-CF_x cell would therefore be expected to follow the kinetics of this decomposition reaction. One might also assume that this reaction is slow enough to observe using microcalorimetry.

This work investigates the thermal powder behavior of Li-CF_x cells under intermittent discharge to try and observe the kinetics of the decomposition reaction. The thermal power behavior was also studied as a function of depth of discharge and rate of discharge with three different CF_x materials. The commercially available CF_x materials evaluated in this work were prepared by high temperature fluorination of coke, carbon black, and carbon fiber precursors. The chemical compositions were similar with total fluoride contents in the range of 62.5–64.5 wt% (CF_{1.05} – CF_{1.15}). The materials have different physical properties such as true density, particle size, surface area, and decomposition temperature.

2. Experiment

CF_x materials were obtained from Advanced Research Chemical and were designated ARC 1000 (coke), ARC 2065 (carbon black), and ARC 4000 (carbon fiber). Table 1 gives the physical and chemical properties of the materials. Cathodes were prepared by mixing CF_x, PVDF, carbon black, dibutylphthalate, and acetone in a stainless steel blender cup. The slurry was cast on glass and dried in air. The plasticized films were laminated to treated aluminum grids and then

extracted in methanol. The extracted cathodes were 75% CF_x, 10% carbon black, and 15% PVDF. Cathodes were dried under vacuum at 105 °C for 2 hr before use. Cells were constructed from coin cell hardware using 0.020 in lithium, 2 layers of Celgard separator, and 1M LiBF₄ propylene carbonate: 1,2-dimethoxyethane electrolyte. Cells were crimp sealed, the impedance was measured, and cells were placed in an aluminum cell holder that provides improved heat transfer from the cell to the microcalorimeter. The aluminum holder was electrically insulated from the metal microcalorimeter chamber using several thin sheets of mica and non-conductive heat sink compound. The cell holder was at the bottom of a battery testing insert that fits into the microcalorimeter and that has 3 thermal breaks and a thin channel used to get leads from the microcalorimeter to the Maccor Series 4000 tester. The microcalorimeter is a Calorimetry Sciences Corporation Model 4400 Isothermal Microcalorimeter operating at a nominal 25 °C. The practical resolution of this microcalorimeter was ±10 μW and this limited the low end of the discharge rate regime chosen. The cells were allowed to equilibrate for 12 hr in the microcalorimeter and then they were discharged approximately 10% of their full capacity, at rates between 5 and 40 mA/g, and then allowed to rest at open circuit for 3 hr before the next discharge. Cells were discharged multiple times until all of the capacity was removed or the voltage dropped below 2.0 V.

Table 1. Physical and chemical properties of CF_x materials tested.

Property	ARC 1000	ARC 2065	ARC 4000
Carbon Source	Petroleum Coke	Carbon Black	Carbon Fiber
Total Fluoride %	62.6	64–65	63.5
Color	Light Gray	White	Light Gray
Median Particle Size, mm	8	< 1	6
BET Surface Area, m ² /g	139	350	323
Micropore Surface Area, m ² /g	78	82	92
External Surface Area, m ² /g	61	268	230
Decomposition Temp., °C	672	660	659

3. Results and Discussion

Figure 1 shows discharge curves for the coke based CF_x material at four different rates. The spikes in the voltage are the 3 hr rest periods between each 10% discharge. The results show a material that has a small but significant change (130 mV) in running potential as a function of a large change in discharge rate (5–40 mA/g). The electronic resistance of the cell was calculated from the 10 ms voltage change that occurs before and after each rest period. The voltage drops were usually 10–20 mV which does not account for the 130 mV shift seen. This indicates that although there is some effect on cell polarization due to the strictly electrical resistances of the

cell, another factor is leading to the larger polarization seen between the OCV at 3.1 V and the running potential at 2.5–2.6 V.

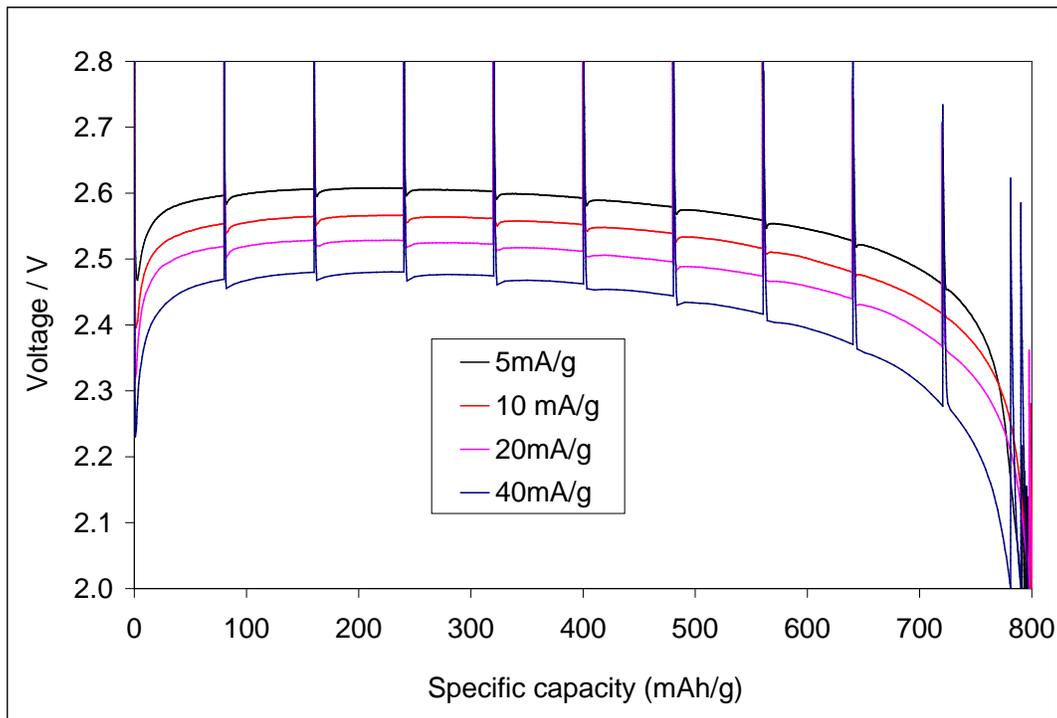


Figure 1. Voltage versus specific capacity of Li-CF_x cells at four discharge rates.

Figure 2 shows the discharge voltage and microcalorimeter response as a function of time for a cell discharged at 20 mA/g. In this figure, the 3 hr rest periods are obvious. The figure shows that the thermal power generated by discharge mirrors the electrical power delivered by the cell almost exactly. The data in figure 2 also allows for the calculation of the I^2R heat from the 10 ms voltage drops. The I^2R heat averages 28 μW , only about 1% of the total thermal power output from the cell. Figure 3 shows an overlay of the thermal power curves for each successive pulse from the data in figure 2, with the first and last pulse left out for clarity. The data shows that heat generation begins immediately upon discharge and reaches 98% of its steady state value within 20 min. The heat generation ceases immediately when discharge is stopped, with 98% of the steady state value being reached within 25 min. This indicates that if a ternary intercalation phase forms, it decomposes extremely rapidly. These 20 min lag times are consistent with the measured time constant of the microcalorimeter itself and, therefore, are not an indication that an intercalated phase persists. The time for the cell potential to reach a steady state value is 5 min on discharge. After discharge ceases, the cell does not reach a steady state open circuit voltage even after 3 hr. It appears that the open circuit potential and the heat generation are not correlated.

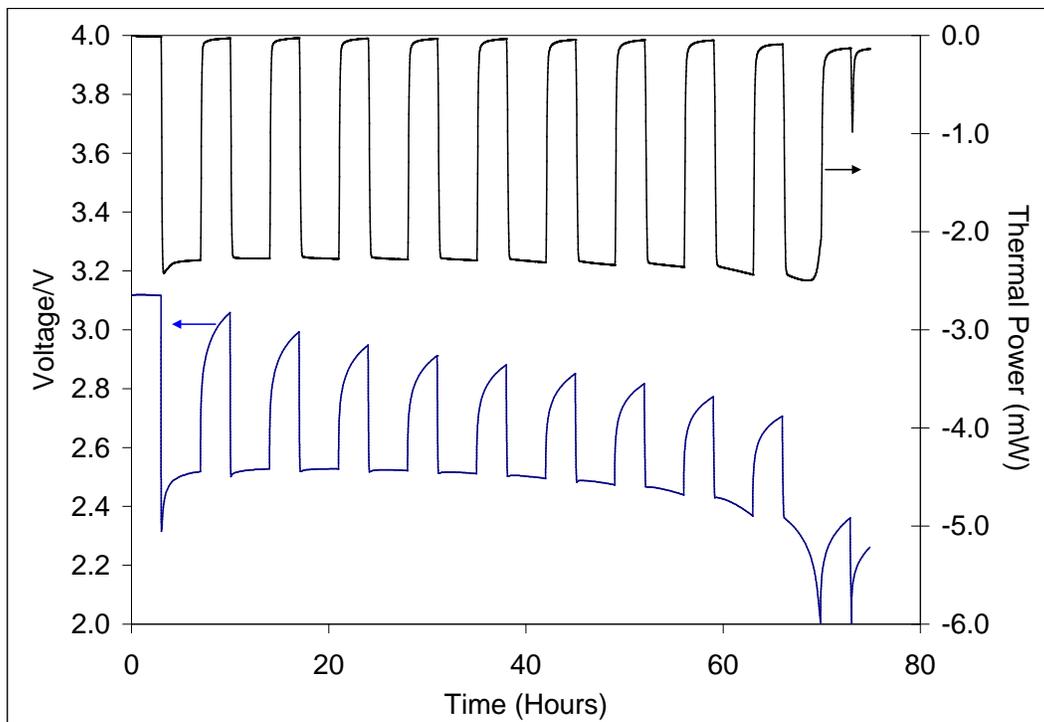


Figure 2. Li-CF_x cell voltage and thermal power (mW) versus time for 20 mA/g discharge rate.

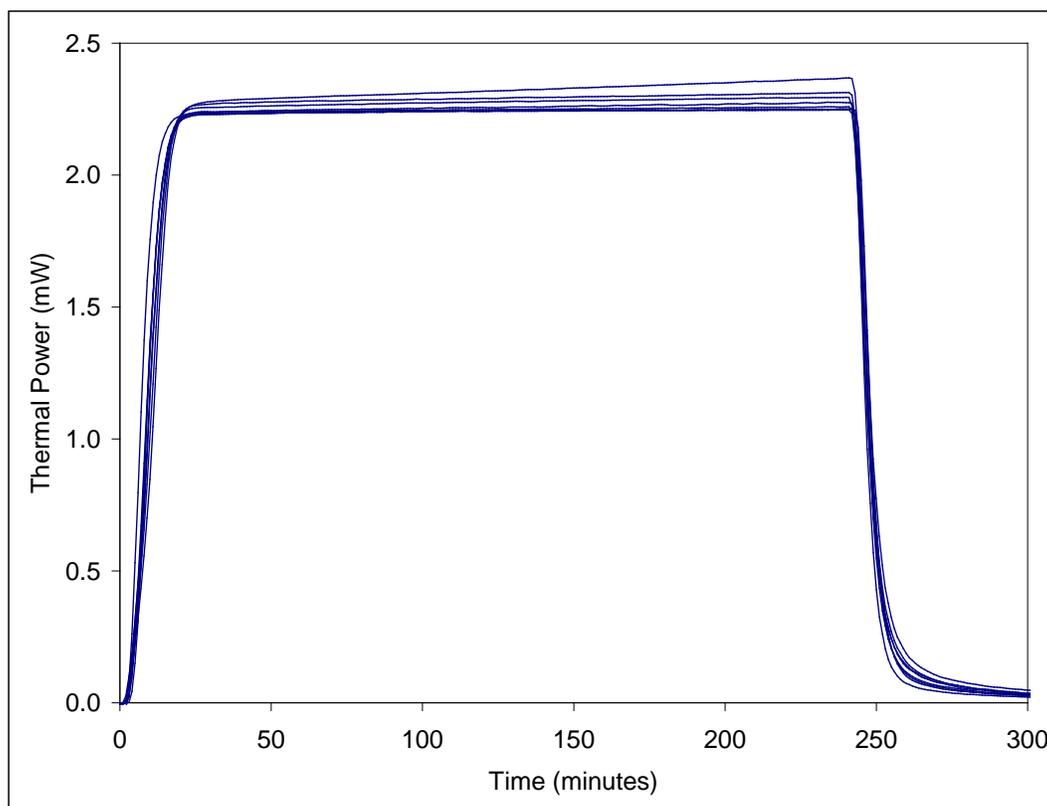


Figure 3. Overlay of thermal power during each discharge pulse for the 20 mA/g discharge rate.

One interesting aspect of the data is how the thermal power is nearly independent of discharge state. Figure 4 shows the thermal power for each discharge step normalized to the weight of CF_x in the cathode. One can see small changes in the thermal power output at the beginning and the end of discharge that are reflected in the cell polarization, but otherwise it is constant. This constancy points to a 2 phase reaction mechanism for discharge where no significant amount of intermediate phase forms.

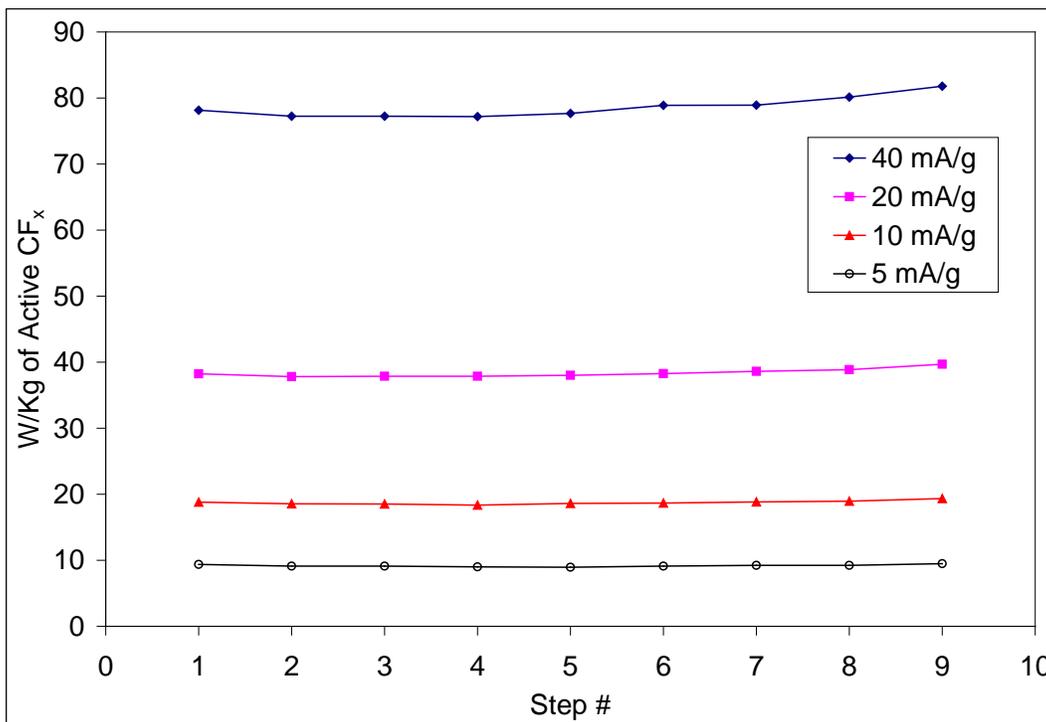


Figure 4. W/kg of active CF_x material at 40, 20, 10, and 5 mA/g.

Table 2 summarizes the discharge data and also gives values for quantities calculated from the data. The running voltage is taken from the curves in figure 1 and represents the highest point on the discharge curve. The heat in J/mAh is calculated by integrating the thermal power curves over time. The theoretical OCV is obtained by first calculating ΔG from the heat in KJ/mol e^- and $T\Delta S$, where ΔS is taken from Wood, et al. (1) for the reaction of Li and $CF_{1.0}$. This value is converted into a potential using $\Delta G = nFE$ and added to the running potential and the 10 ms IR drop to get a theoretical OCV. These OCV values agree well with the values of Wood et.al. (1).

Table 2. Summary of values from calorimetry and discharge data.

Rate (mA/g)	40	20	10	10	5
Average J/mAh	7.08	6.89	6.68	6.74	6.55
Heat (KJ/mol e^-)	186.7	178.7	178.7	179.1	174.8
Running Voltage	2.479	2.574	2.574	2.566	2.608
Theoretical OCV	4.470	4.466	4.466	4.467	4.463

As stated before, the change in cell polarization with discharge rate is not related purely to the electrical resistances in the cell, as this can account for only 20 mV of polarization even at 40 mA/g. Most of the cell polarization is related to the overpotential associated with the discharge reaction. When the change in heat output between different discharge rates is converted to a voltage using $\Delta G = nFE$, the voltage drop seen between cells at different rates can be accurately predicted. In addition, when the heat in KJ/mol e^- is plotted against running potential, one obtains figure 5. The data falls on a straight line that, when extrapolated back to zero heat, results in the theoretical OCV for the Li/CF_x system of 4.2 V. This result would mean that both the running potential and the OCV are the result of a large activation barrier for discharge, and that the polarization seen as a function of discharge rate is simply an extension of this.

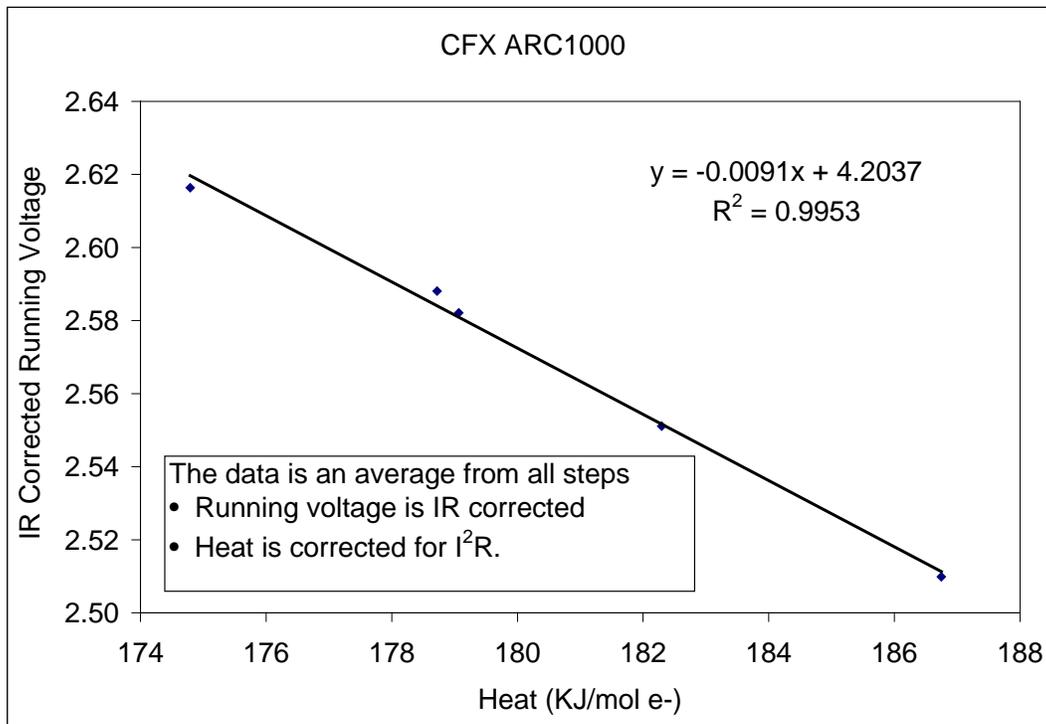


Figure 5. Correlation between running voltage and heat output in KJ/mol e^- .

The other CF_x materials, ARC 2065 and ARC 4000 were tested under conditions identical to the ARC 1000 material with the results for the 40 mA/g rate shown in figure 6. The ARC 2065 material shows less polarization on average than the ARC 1000 material with lower Joules/mAh. The ARC 4000 material shows more polarization than the ARC 1000 material, but interestingly lower Joules/mAh as well. Plots of running voltage against heat in KJ/mol e^- give results similar to figure 5 with linear fits for both the ARC 2065 and ARC 4000 materials. The theoretical OCV by extrapolation for the ARC 2065 material was 4.32 V and for the ARC 4000 material was 4.20 V. The difference in thermal behavior between the three materials is relatively small, about 1–

2% depending on how it is calculated. A graph incorporating all of the data shows that the three materials occupy a range of heat/capacity values between 6.3 and 7.0 J/mAh depending on discharge rate with only one exception, the 5 mA/g ARC 2065 cell, falling outside this range. This result would be surprising if one assumes that the discharge reaction takes place through the formation of an intercalate, since it is expected that physical properties such as surface area and particle size should influence the intercalation kinetics. The result is more understandable if one assumes that discharge takes place through a two phase reaction, as this will depend mainly on the chemical properties of the materials.

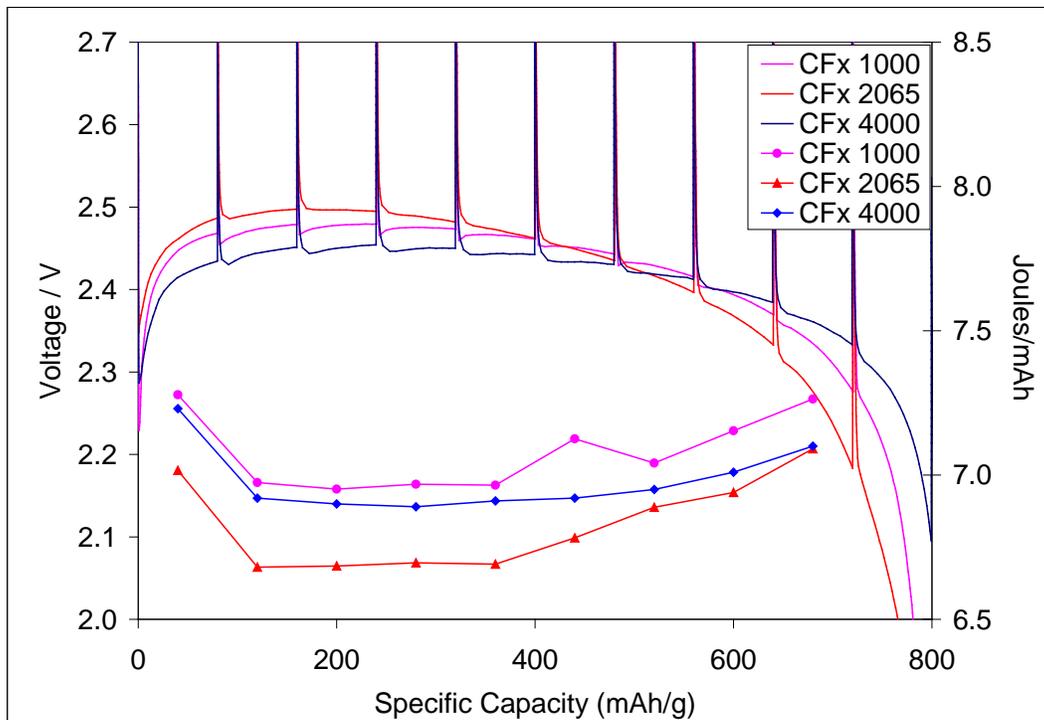


Figure 6. Voltage versus specific capacity and J/mAh. Comparison of ARC 1000, ARC 2065, and ARC 4000 at 40 mA/g.

4. Summary and Conclusions

This study shows that the thermal power of Li-CF_x cells is highly rate dependent, but nearly independent of the state of discharge. Intermittent discharge data shows how heat generation starts immediately when discharge begins and ceases almost as quickly when discharge is stopped. There is no significant tail in the thermal power curve that could be interpreted as the decomposition of an intercalation compound. Extrapolation of the running potential versus heat to a zero value results in an OCV of 4.25 V, very near the theoretical potential calculated by Wood et al. (1). The calorimetry results on three physically different CF_x materials turn out to be

nearly identical. This shows that physical properties, such as surface area and particle size, have almost no effect on the heat produced and that chemical composition is probably more important. The results of this study suggest that the discharge mechanism is simply a two phase reaction where the large activation energy needed to break C-F bonds results in significant overpotential on discharge.

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