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Performance Evaluation of Commercial CF_x Materials in Lithium Batteries

by Jeffrey Read, Michelle Marx, Jeffrey Wolfenstine, Sheng Zhang, and Don Foster

ARL-TR-5001 **October 2009**

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED (From - To)
October 2009	Summary	May 2008 to July 2009

4. TITLE AND SUBTITLE
Performance Evaluation of Commercial CF_x Materials in Lithium Batteries

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Jeffrey Read, Michelle Marx, Jeffrey Wolfenstine, Sheng Zhang, and Don Foster

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
ATTN: RDRL-SED-C
2800 Powder Mill Road
Adelphi, MD 20783-1197

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-5001

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The performance of six different commercially available carbon monofluoride (CF_x) materials were evaluated at four different discharge rates. The physical and chemical properties of the CF_x materials were correlated to cell performance in lithium coin cells. This study was undertaken to determine if there are specific physical or chemical properties that can be tied to performance and if modification of these properties could lead to an improved carbon monofluoride material.

15. SUBJECT TERMS
CFx, lithium batteries, physical properties, electrochemical properties

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE	UU	16	Jeffrey Read
Unclassified	Unclassified	Unclassified			19b. TELEPHONE NUMBER (*Include area code*) (301) 394-0313

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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 been shown to have the rate capability necessary for Soldier applications (*1–4*). Voltage delay at low temperature and heat generation at higher discharge rates (*2, 3*) are existing problems that need to be mitigated.

The overall discharge reaction that takes place in a Li-CF_x cell is shown in equation 1.

$$Li + CF_x \rightarrow C + LiF \qquad E^o = 4.55V \tag{1}$$

The E° value is that given by Wood et al. (*5*) for a $CF_{1.12}$ 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 and actual potential can be explained in several different ways. The first and currently accepted explanation states that there is formation of ternary phases (*6, 7*) such as CLi_xF or $CFLi_x{:}S_y$ where S is a solvent molecule that is co-intercalated with the lithium ion upon discharge. The potential for the formation of this intercalated phase, it is proposed, would be lower than that for direct reaction of lithium with CF_x. The heat generated by a Li-CF_x cell is normally assigned to the heat generated when this proposed ternary phase decomposes to LiF and carbon in a chemical reaction. One alternate explanation for the low OCV is that there is a large activation energy and therefore large overpotential associated with breaking any C-F bond, especially the covalent C-F bonds found in commercial CF_x battery materials. This large activation energy would also lead to poor kinetics during discharge and significant heat.

The purpose of this work was to investigate how the physical and chemical properties of commercial CF_x materials affect discharge capacity, discharge voltage, rate capability, and voltage delay in Li-CF_x cells. A variety of commercially available CF_x materials were evaluated in this work. The chemical compositions of the various materials are similar with total fluoride contents in the range 60–65 wt% ($CF_{0.95}$–$CF_{1.15}$). These CF_x materials are prepared from different starting materials such as cokes, graphites, carbon fibers, and carbon blacks, and have different physical properties such as particle size, surface area, and decomposition temperature.

2. Experiment

CF_x powders from Advanced Research Chemical (Catoosa, OK) and Lodestar (Howell, NJ) were used as received. The decomposition temperature for each material was measured on a Perkin Elmer TGA 7 at a heating rate of 5 °C/min under N_2 atmosphere. Surface area measurements

using N_2 absorption were carried out on a Micromeritics ASAP 2010 after degassing samples at 250 °C. Particle morphology was characterized using optical microscopy.

Cathodes were prepared by mixing CF_x, PVDF, carbon black, dibutylphthalate (DBP), 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 extracted in methanol to remove the DBP. The cathode composition after extraction was 75 wt% CF_x, 10 wt% carbon black, and 15 wt% PVDF. Cathodes were dried under vacuum at 105 °C for 2 hrs before use. Cells were constructed from 2035 coin cell hardware using 0.020 inch thick lithium foil, 2 layers of Celgard separator, and 1M $LiBF_4$ propylene carbonate:1,2-dimethoxyethane (1:1 wt/wt) electrolyte. Cell impedance and OCV was measured for each cell before being placed on test.

The cells were allowed to equilibrate for 3 hrs at 20 °C before being discharged at rates of 5, 10, 20, and 40 mAh/g. The discharge was tailored to the cathode weight of each cell to insure that any differences in cathode density or thickness were minimized. Cells were discharged until all of the capacity was removed or the voltage dropped below 2.0 V.

3. Results and Discussion

The CF_x materials commonly used in batteries are prepared from either coke or carbon fiber which is then fluorinated at high temperature. ARC 1000 and Fluorstar PC/10 are produced from coke while ARC 4000 and Fluorstar F are prepared from carbon fiber. Several CF_x materials typically used for lubrication purposes were also evaluated in this study, one prepared from graphite (ARC 3000) and one from carbon black (ARC 2065). Table 1 shows the properties of each of the materials tested. Carbon source, total fluoride %, and median particle size are reproduced in the table from the suppliers data sheets while the remaining properties were measured here. One can see that the total fluoride % is typically 60–65% for these materials. This corresponds to a carbon to fluorine ratio of around 1.0. The color of the various CF_x materials reflects the total fluoride % with ARC 3000, the material with the lowest fluoride content, being dark grey and ARC 2065 with the highest fluoride content, being pure white.

Table 1. Chemical and physical data on CF_x powders.

	ARC 1000	**ARC 2065**	**Product ARC 3000**	**ARC 4000**	**FluorStar PC/10**	**FluorStar F**
Carbon Source	Petroleum Coke	Carbon Black	Graphite	Carbon Fiber	Coke	Carbon Fiber
Total Fluoride %	62.6	64–65	60.4	63.5	61–62	61–63
Color	Light Gray	White	Dark Gray	Light Gray	Light Gray	Light Gray
Median Particle Size, μm	8	<1	2	6	8	8
BET Surface Area, m^2/g	139	350	109	323	170	340
Micropore Surface Area, m^2/g	78	82	52	92	102	96
External Surface Area, m^2/g	61	268	57	230	68	244
Decomposition Temp., °C	672	660	640	659	672	700

Sources:
ARC (Advanced Research Chemical)
FluorStar (Lodestar)

The BET surface areas measured here and given in table 1 correspond well with those from the data sheets provided by the manufacturers. In addition to the total BET surface area, our measurements also give values for the surface area due to micropores. Table 1 shows that for all of these materials, there is a significant contribution to the surface area (50–100 m^2/g) from these micropores. According to the BET data, these micropores have an average diameter of 25–50 angstroms. The micropores are formed during the fluorination process as some of the carbon material is converted to CF_4 gas or other volatile CF_n compound.

The decomposition temperature we measured using TGA is typically higher than that given by the manufacturer, if a number was given. We assume that this is due to the fact that we are using a different atmosphere (N_2 vs. air) and to the analytical method used to extract the onset temperature. We were consistent in our determination method such that a comparative analysis could be made even if the absolute value can be in dispute.

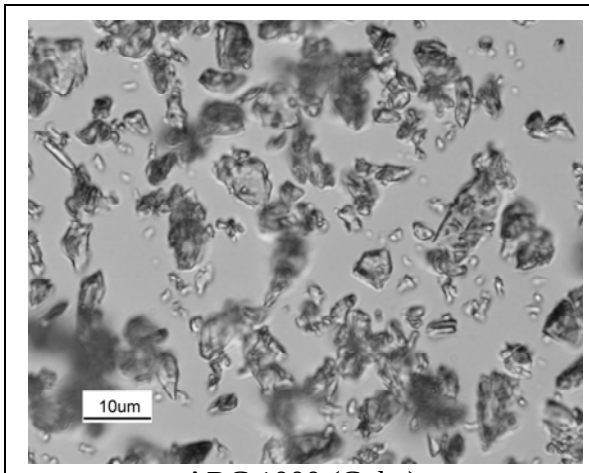
Figure 1 shows the optical microscope images for the various powders, confirming the particle size and morphology for the materials. The ARC 2065 powder is extremely small, certainly smaller than 1 μm. The ARC 1000 material appears to have particles up to 10 μm in size while the ARC 3000 material has a maximum particle size of about 4 μm. The ARC 4000 material has particles that are possibly up to 12 μm in width but with lengths up to 100 μm. The particle size as seen in the optical images correlates well with the values given by the manufacturers.

Figures 2 and 3 show the discharge curves of the various CF_x materials at both 5 mA/g and 40 mA/g. With the exception of the ARC 3000 material, all have very similar discharge profiles and specific capacities. The curves demonstrate the two phase nature of the discharge with a very flat voltage profile. From figures 2 and 3, one can see that the ARC 3000 material has 20% lower capacity than any of the other materials and a more sloping discharge curve. From table 1, the two obvious differences between this material and the others are that the total fluoride % and the

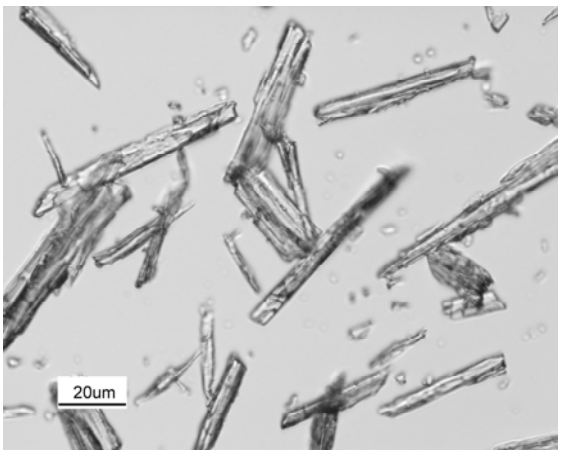
decomposition temperature is the lowest of any of the materials tested. This lower fluoride content can account for only about half of the capacity decrease, while both the lower fluoride content and the lower decomposition temperature points to a material that has some ionic CF bonds, that is it is subfluorinated and could account for the sloping discharge profile seen in this material.

Figures 4 and 5 show how the specific capacity and peak voltage vary with rate for the different materials. From the data in table 1, it appears that particle size has a significant affect on actual running voltage. The smallest particle size materials have the highest running potential. The particle size of the ARC 2065 material is in fact less than 1 μm. Given that the discharge reaction can be characterized as a two phase reaction, small particle size should lead to lower electrode polarization since the electrochemical interface becomes significantly larger as the particles become smaller.

The voltage and rate performance does not appear to correlate with BET, external, or micropore surface area. Table 1 shows that both ARC 1000 and Fluorstar PC/10 have higher micropore area and higher external surface area when compared to ARC 3000, yet this material has a significantly higher running potential. In addition, ARC 2065, ARC 4000, and Fluorstar F have almost identical BET surface areas, yet their running potentials are significantly different, as shown in figure 2. It would appear that the small size of the micropores and the surface roughness that leads to the high surface area does not result in either higher running voltage or better rate capability in these materials. It could be that these micropores and surface features are too small to be part of the electrochemical interface during discharge.



ARC 1000 (Coke)



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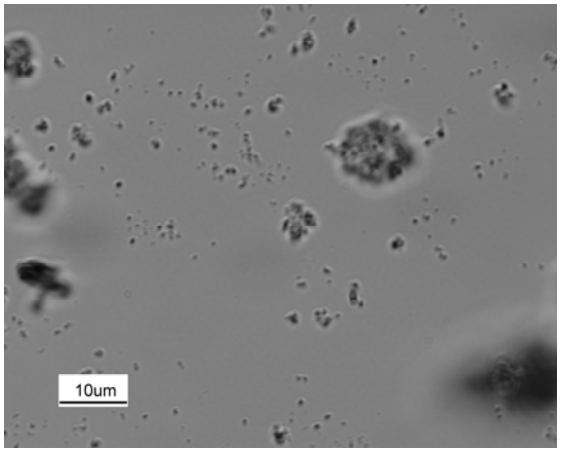
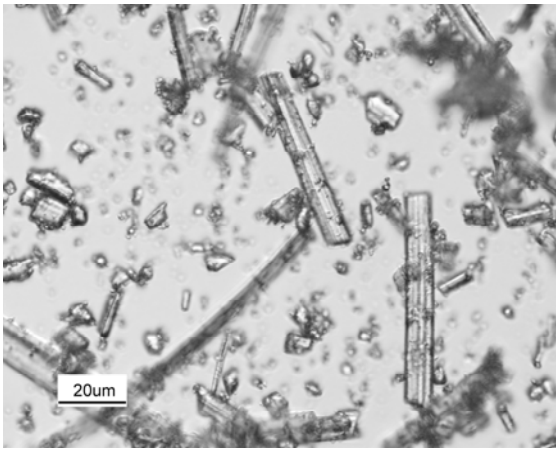
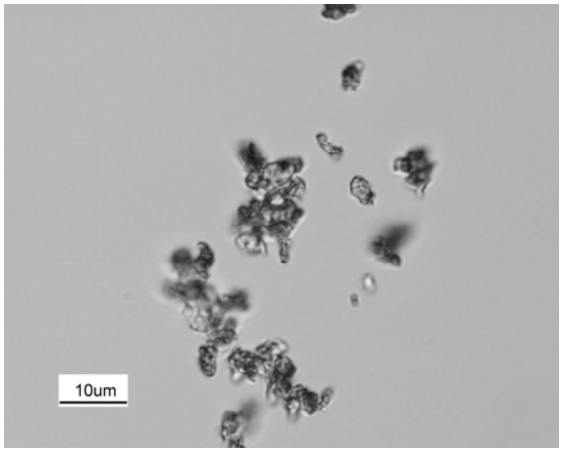


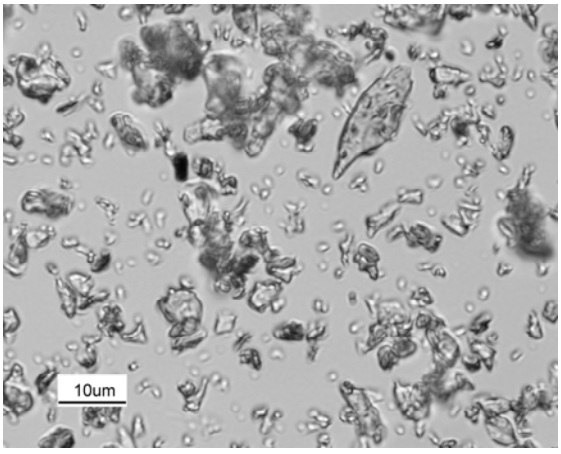
ARC 2065 (Carbon Black)



Fluorstar Type F (Carbon Fiber)



ARC 3000 (Graphite)



Fluorstar PC/10 (Coke)

Figure 1. Optical microscope images of CF_x powders.

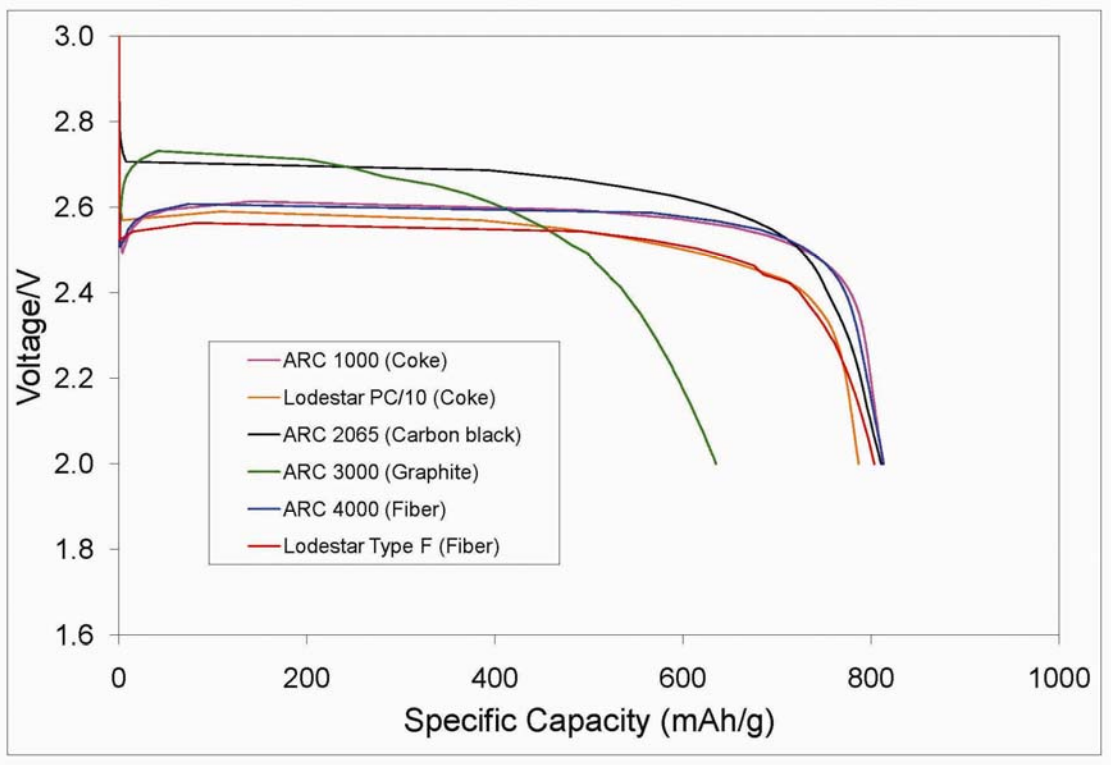


Figure 2. Voltage profiles at 5 mA/g.

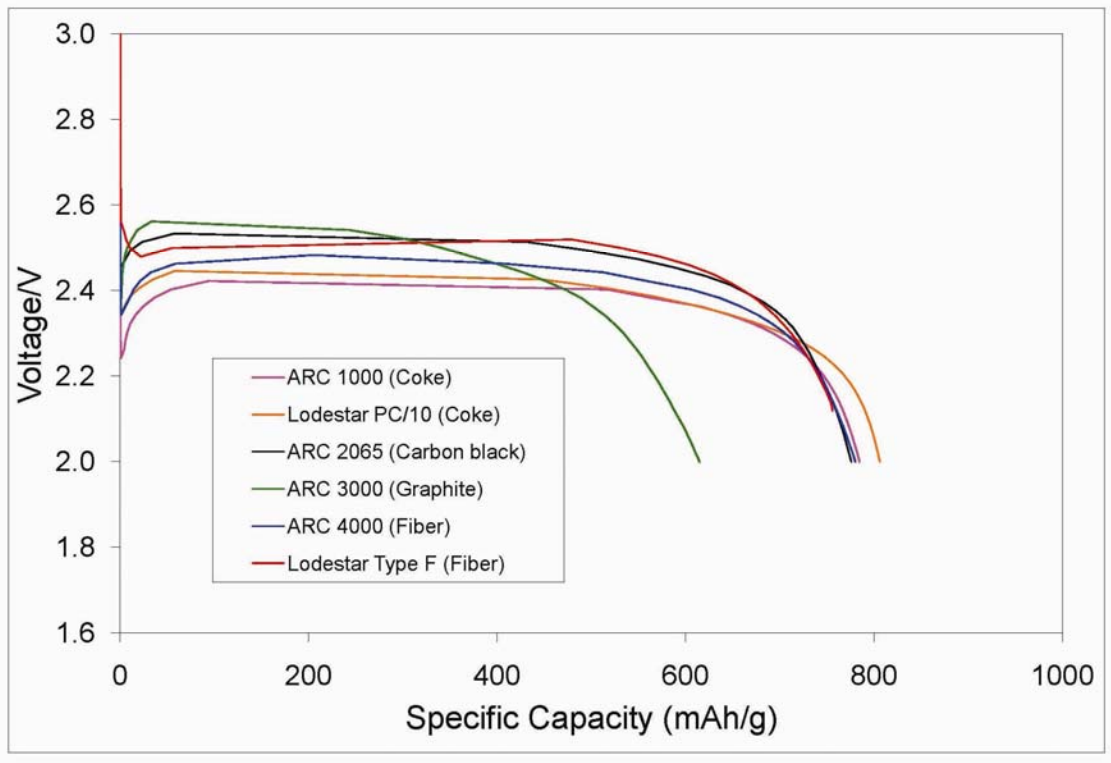


Figure 3. Voltage profiles at 40 mA/g.

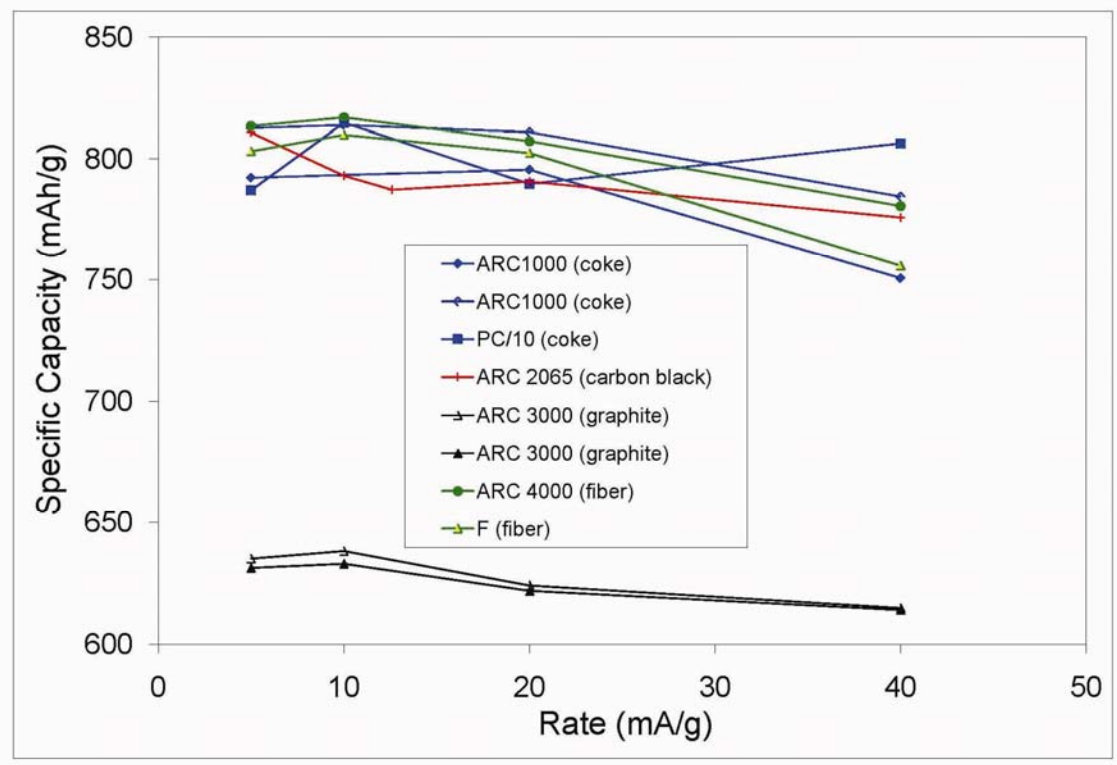


Figure 4. Specific capacity versus rate.

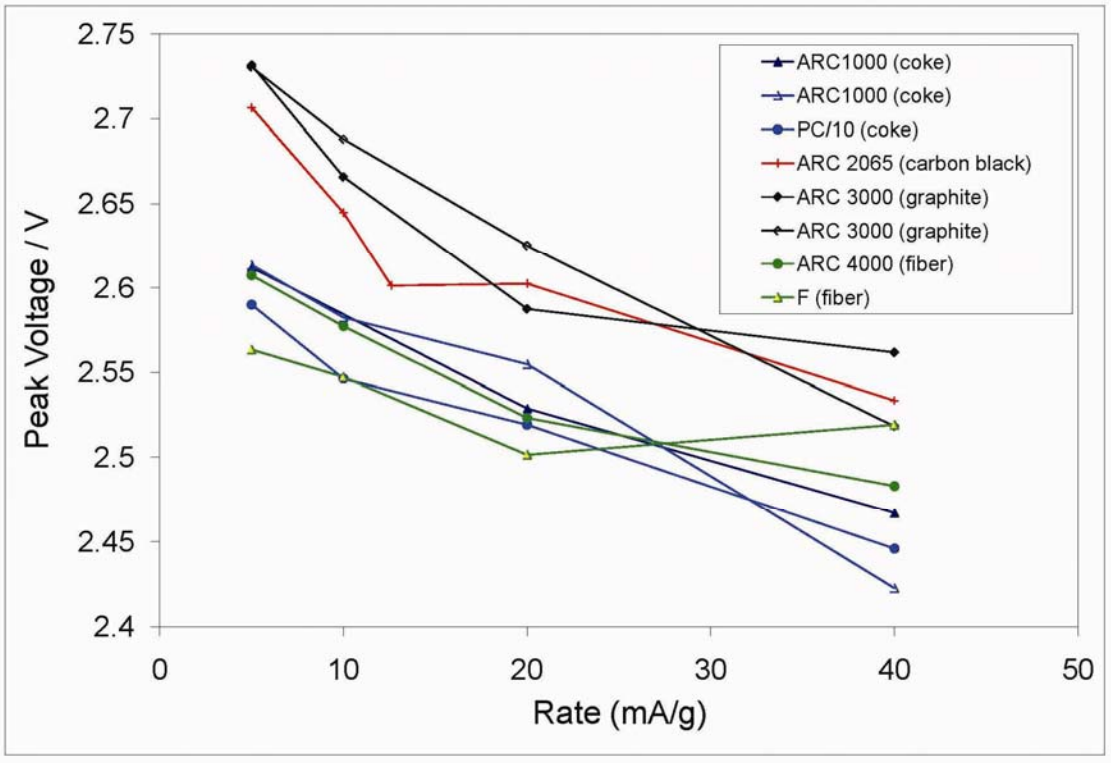


Figure 5. Peak voltage versus rate.

4. Summary and Conclusions

The performance of six different commercially available carbon monofluoride (CF_x) materials were evaluated and it was found that most give a discharge profile that can be interpreted as a 2 phase discharge. The materials have similar specific capacities, except for ARC 3000 which has a discharge capacity that is 20% lower. This lower capacity can be accounted for at least partially by the lower fluoride content. The main physical property that can be tied to performance is the particle size, with smaller particle sizes giving less overpotential and higher running voltage. The ability to produce a nanosized CF_x might be one approach to increase the running potential of Li/CF_x cells. ARC 2065 performs as well as the battery grade materials in terms of specific capacity and might be considered as an additive to commercial batteries to increase rate or voltage performance.

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