

SAFETY OF CARBON MATERIALS FOR LITHIUM-ION BATTERIES

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Introduction

Lithium-ion batteries, currently the state-of-the-art power sources for laptop computers and cellular phones, are being considered for powering electric vehicles (EVs). Chemical reactions between the electrode materials and the electrolyte of Li-ion batteries occur at high temperature under conditions of mechanical or electrical abuse [1,2]. Previous work on the reactions occurring at high temperatures has demonstrated that the reaction between lithium-containing carbon and electrolyte is detected first, as cells are heated [2,3,4,5,6]. Hence, this reaction plays an important role in determining cell safety.

The major manufacturers of Li-ion cells use different carbon sources. It is important to understand whether the reaction between lithium-containing carbon and electrolyte at high temperature depends on the carbon type. In this work six different carbons, differing in morphology, heat-treatment temperature and surface area were studied. All carbons had a detailed structure refinement [7], BET surface area measurements and SEM images performed and their results are shown in table 1 and figure 1.

Experimental

Samples of lithium-intercalated carbons were prepared in 1M LiPF₆ EC:DEC (33:67) as described in [2]. Three synthetic graphites, KS-75, SFG-44 and SFG-75 (Timcal), XP-3 petroleum coke (Conoco), and heat-treated MCMB (Osaka Gas) and carbon fiber (BP Amoco pitch) were studied. The cells were fully discharged to 0.0V and then prepared for analysis in an accelerating rate calorimeter (ARC) as described in [2]. The ARC is an adiabatic calorimeter that sequentially heats to a temperature and then searches for an exotherm (0.02°C/min). When an exotherm is detected the self-heating of the sample is tracked by matching any increase in the sample temperature with an identical increase in the temperature of the calorimeter, ensuring adiabatic conditions are met. This tracking is continued until the stop temperature (220°C) was reached.

Results and Discussion

The self-heating rate profiles of the various lithium-containing carbon samples as a function of temperature is given in figure 2. The results can be

classified into two groups: the high surface area synthetic graphites that exhibit a large self-heating rate and the low surface area MCMB and fiber in addition to the coke that exhibit a lower self-heating rate. It is clear that it would be difficult to prepare Li-ion cells which do not exhibit thermal runaway under abuse conditions with high surface area synthetic graphites.

Previous work with the ARC [2] has shown that the initial temperature rise (labeled as ΔT in figure 2 for one sample) is due to the decomposition of the solid electrolyte interface (SEI). Figure 3 demonstrate that as the amount of SEI increases (more surface area), the initial temperature rise, ΔT , also rises. XP-3 coke does not fit this description and further experiments are being conducted to address this "coke anomaly".

It has been shown [2] that the initial part of the self-heating profiles obtained upon heating nominal samples to higher initial starting temperature can be fit to a straight line, where one can extract kinetic parameters from a typical Arrhenius-type plot. The results of such an analysis are given in table 1. The activation energies of the decomposition of the SEI for all the samples are very similar and this suggests that the heat generating reactions are the same in each of the carbons only the extent of the reaction varies.

Conclusion

The similarities of the reaction(s) occurring at elevated temperature between lithium-intercalated carbons and LiPF₆ EC:DEC (33:67) electrolyte has been demonstrated. The initial process shows an activated behavior associated with the decomposition of the SEI with energy of about 1.4 eV. The reaction rates for the decomposition of the lithium-intercalated carbon material increases with the surface area of the graphitized samples, while the XP coke sample has a self-heating rate that is lower than expected based on its surface area.

The results presented here provide a good indication as to the direction to follow for improved thermal stability in carbon anodes, which will ultimately lead to an increase in cell safety. Taking into account the characteristics required for anode materials, such as capacity, charge retention, and thermal stability, two carbon morphologies, spheres and fibers appear to excel over the others. The disadvantage of the fiber studied here is its shape, which leads to electrodes of low density. If the fibers could be packed more efficiently, then they

would be good candidates for the anodes of Li-ion cells. Given the control that exists over the fiber diameter and length in the manufacturing process we feel that carbon fibers may ultimately offer the optimum geometry for safety and performance of lithium-ion battery anodes.

References

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Table 1: Summary of experimental results

Carbon	Lattice Constants (Å)		Random Stacking Prob. (± 0.02)	Irr. Cap. (mAh/g)	Surface Area (m ² /g) (± 0.2)	ΔT (°C)	Ea (eV) (± 0.1)	A (min ⁻¹) (± 10%)
	a (±0.002)	c/2 (±0.002)						
MCMB	2.457	3.362	.19	50	0.8	16 ±2	1.4	4.7 x 10 ¹⁶
SFG-75	2.461	3.358	.04	50	3.5	34 ±4	1.5	6.4 x 10 ¹⁷
SFG-44	2.460	3.357	.04	50	4.3	37 ±4	1.5	1.6 x 10 ¹⁸
KS-75	2.459	3.355	.10	57	9.2	50 ±5	1.3	1.8 x 10 ¹⁶
XP3	2.440	3.445	1.0	50	6.7	18 ±2	1.5	1.8 x 10 ¹⁸
Fiber	2.457	3.357	.26	33	0.4	10 ±2	1.5	3.7 x 10 ¹⁸

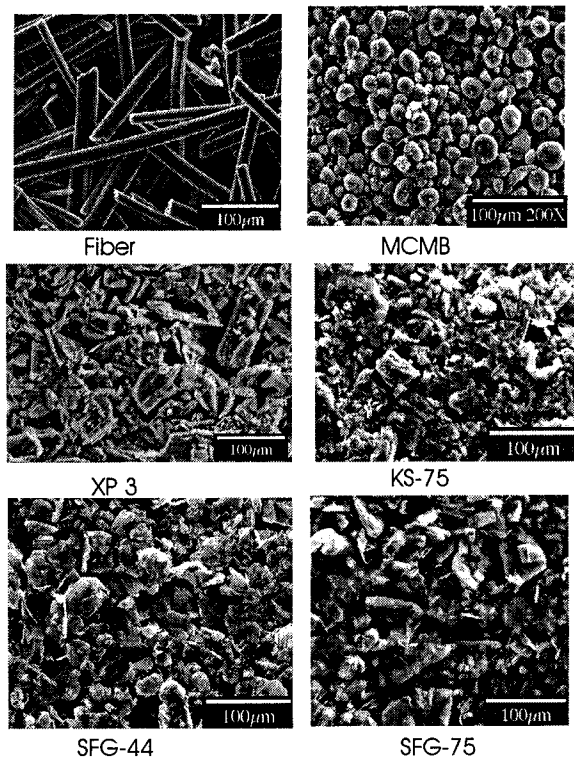


Figure 1. Scanning electron micrograph of each of the carbons under study.

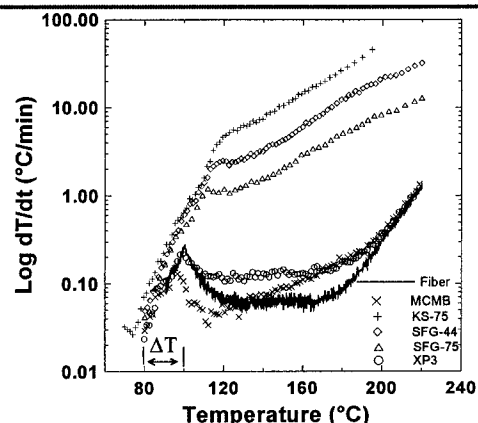


Figure 2. Self-heating rate profiles of lithium-intercalated carbons in LiPF₆ EC:DEC (33:67) electrolyte.

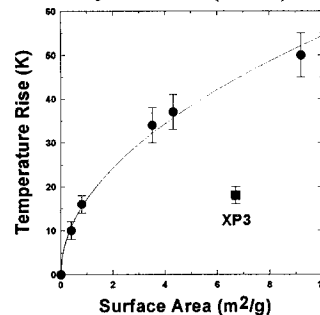


Figure 3. Initial temperature rise, ΔT, of the carbons under study as a function of surface area