

Comparative thermal stability of carbon intercalation anodes and lithium metal anodes for rechargeable lithium batteries

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Abstract

An accelerating rate calorimeter has been used to probe the thermal stability of Li_xC_6 in electrolyte as a function of specific surface area, lithium content, and solvent choice. The exotherm can be qualitatively modelled based on the reaction which produces the passivating film on the carbon surface.

Keywords: Thermal stability; Safety; Lithium anode; Carbon anodes; Rechargeable lithium batteries

1. Introduction

Although good safety characteristics are essential for a commercial product, this aspect of the rechargeable lithium battery has historically received scant attention from the scientific community. This paper will focus on the thermal stability of the carbon anode and how it relates to cell safety. We show that replacing the lithium metal with a carbon intercalation anode improves the fundamental safety of cells, and also makes the safety of cells more predictable. Because of this, the lithium metal anode in rechargeable lithium cells has been supplanted by the Li_xC_6 intercalation anode. Lithium-ion cells with carbon anodes, which have been on the market for more than two years, have established a good safety record [1,2].

Most abusive conditions (e.g., short circuit, crushing, etc.) lead to heating of the cell. Safety problems arise if for any reason the cell exceeds the critical temperature above which thermal runaway occurs. Thus, the thermal stability of the entire cell and various combinations of cell components are a key to understanding and improving cell safety.

2. Accelerating rate calorimeter

We have used an accelerating rate calorimeter (ARC, Columbia Scientific Instruments) to carefully probe the

thermal stability of the coke electrode as a function of specific surface area, lithium content, and choice of electrolyte. The ARC is a sensitive adiabatic calorimeter which tracks the temperature of reactive samples as they self-heat. Samples are brought to the desired starting temperature, then checked for self-heating during a 10 min equilibration period. If the self-heating rate (dT/dt) exceeds a threshold level of $0.02\text{ }^\circ\text{C}/\text{min}$ the instrument remains in the adiabatic mode and follows the exotherm. When dT/dt drops below the threshold level, the temperature is increased in $10\text{ }^\circ\text{C}$ steps until another exotherm is detected, or until the designated upper temperature limit is reached. To increase the sensitivity of the instrument and to permit loading of solid samples, light-weight steel cans were used as sample containers. The cans used as ARC sample containers were hermetically sealed by tungsten inert gas welding under argon, and were loaded in an argon-filled glove box to avoid decomposition of Li_xC_6 in air. The instrument and the general theory of operation are described in greater detail by Townsend and Tou [3].

3. Lithium metal anode

The hazards associated with lithium metal anodes are apparent when cycled cells are subjected to mild thermal abuse in a 'hot box'. This test consists of placing cells in a preheated gravity convection oven, then monitoring the cell's surface temperature and open-

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circuit voltage. The cells are not heat sunk in any way. The data presented here are for fully charged AA-size Li/MnO₂ cells prepared by cycling at low rates ($\pm C/10$), which makes them particularly sensitive to thermal abuse.

Fig. 1 shows the thermal response of AA-size Li/MnO₂ cells placed in a 140 °C hot box. The temperature of uncycled (cycle 0) cells approaches 140 °C asymptotically, as would be expected for an inert sample, but cycled cells self-heat and overshoot the oven temperature. The overshoot increases with the number of cycles, until after 25 cycles the cells undergo thermal runaway, emitting intense flame from the pressure vent. The cell voltage remains steady unless cells actually vent, so the self-heating cannot be attributed to internal shorts. The increasing sensitivity to thermal abuse with cycle number clearly implicates the lithium metal anode, since it is the only component that changes appreciably in that its surface area increases upon repeated stripping and plating.

The reactions which lead to runaway self-heating of cells can be studied in greater detail using the ARC. To illustrate the fundamental safety problem associated with the lithium metal anode, we tested the thermal stability of low capacity Li/MnO₂ cells cycled 5, 10 or 25 times at $\pm C/20$ rate. These were spirally wound AA-size cells with oversize mandrels to artificially reduce the cell capacity to about 350 mAh. 1 M LiAsF₆/PC-EC (propylene carbonate-ethylene carbonate) electrolyte was used. The cells were cycled at low rate to encourage the growth of high surface area lithium on the anode.

Fig. 2(a) shows ARC temperature versus time plots for these cells from a starting temperature of 100 °C. To show more detail and to facilitate comparisons between heating rates that can differ by orders of

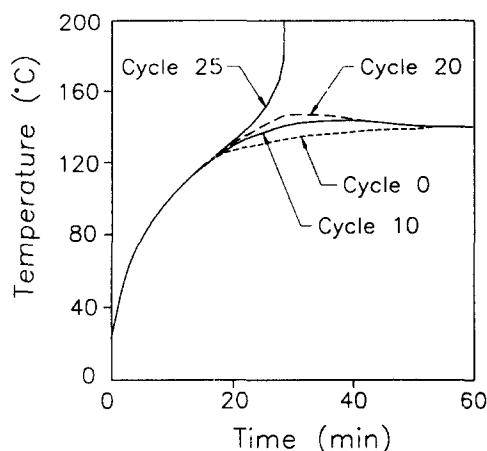


Fig. 1. Temperature response of cycled Li/MnO₂ AA-size cells subjected to 140 °C hot-box test. These cells had a nominal capacity of 600 mAh, contained 1 M LiAsF₆/PC-EC electrolyte and were cycled at 21 °C at a low rate ($\pm C/10$) to promote the formation of high surface area lithium. The number of cycles completed prior to the hot-box test is indicated on the graph; from Ref. [10].

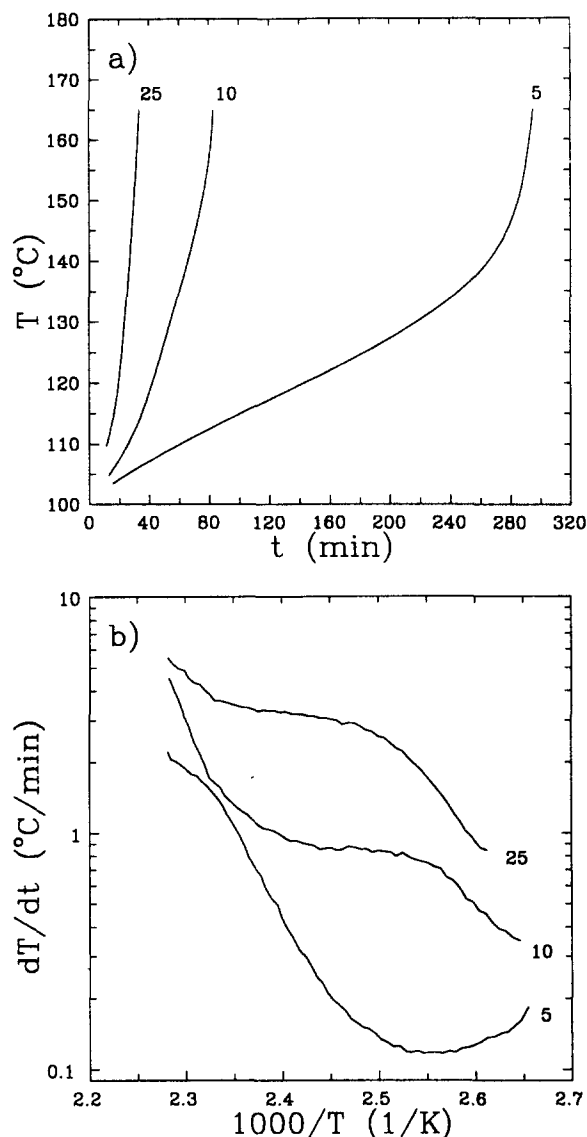


Fig. 2. ARC exotherms of cycled Li/MnO₂ cells starting from 100 °C. these AA-size cells were assembled with oversize aluminum mandrels to reduce the cell capacity to 350 mAh. The cells contained 1 M LiAsF₆/PC-EC electrolyte and were cycled at $\pm C/20$ rates. The number of cycles completed prior to each ARC run is indicated on the graph: (a) shows temperature vs. time, and (b) shows the corresponding Arrhenius plots ($\log(dT/dt)$ vs. $1000/T$).

magnitude, we prefer to present the ARC data as Arrhenius plots as in Fig. 2(b). Fig. 2 shows that the self-heating rate increases dramatically as the cells are cycled, presumably because the specific surface area of the lithium metal anode increases. Thus, cells that are insensitive to thermal abuse when first assembled become more sensitive even under normal operating conditions. We believe that the fundamental problem with the lithium metal anode is that its morphology cannot be controlled, which makes the ultimate safety of cycled cells difficult to predict.

The thermal instability of cells due to lithium/electrolyte reactions, which has been demonstrated by hot-

box and ARC tests, is clearly a cause for concern but one could argue that with suitable protective devices one could prevent cells from ever reaching temperatures above 100 °C. Thus, one might develop a reasonably safe product with a lithium metal anode. However, proving that a lithium metal anode cell is 'reasonably' safe poses a new problem.

Because the morphology of the lithium metal anode cannot be controlled a risk assessment for a particular application requires a statistically significant number of tests covering the full range of possible operating conditions (e.g., temperature, discharge rate, duty cycle). Also, it is essential to test cells over their entire life span, particularly near their end of life where the margin of safety will presumably be lowest. This is a major undertaking which requires testing large numbers of cells. Details of the methodology have been presented elsewhere [5]. Even if the outcome of such a safety testing program is positive, the sheer effort required to prove that cells with lithium metal anodes are safe for a particular application is almost prohibitive. Furthermore, changes in the cell design or operating conditions can affect the anode morphology, and would therefore require additional tests to ensure that product safety has not been compromised.

4. Carbon anode

Unlike lithium metal anodes the morphology of the carbon anode remains essentially constant as the cell is cycled and can be selected at the outset by choosing an appropriate carbon. Fig. 3 shows how the self-heating rate of the lithiated coke (approximate stoichiometry is $\text{Li}_{0.5}\text{C}_6$) depends on the BET surface area of the coke. The Li_xC_6 samples for this study were prepared by equilibrating Conoco XP coke pellets at 0.02 V versus Li in 1 M $\text{LiAsF}_6/\text{PC-EC}$ electrolyte. Thereafter the lithiated carbon pellets were transferred to a AA can in an argon-filled glove box. Additional electrolyte was added and the can was welded shut.

Reducing the specific surface area of the coke clearly improves its thermal stability. Furthermore, we note that while the reaction rate of the lithium anode sample continues to increase with temperature, the reaction rate of low surface area Li_xC_6 samples actually decreases slightly at higher temperatures. Even at 180 °C ($1000/T=2.2$), where lithium metal melts and reacts even more violently, the reaction rate of the low surface area Li_xC_6 remains almost constant.

For comparison the exotherm for the Li/MnO_2 cell with 25 cycles from Fig. 2 has been included. This cell contained approximately three times as much lithium as the Li_xC_6 samples but nevertheless constitutes a valid comparison because this amount of excess lithium is normally required to provide adequate cycle life for

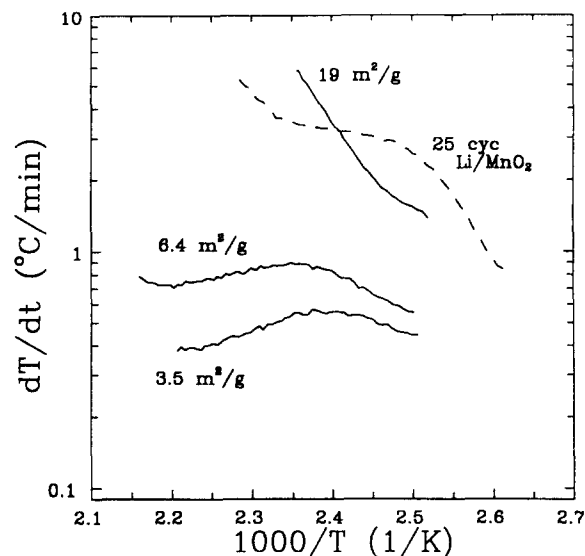


Fig. 3. Effect of coke surface area on ARC exotherms of $\text{Li}_{1/2}\text{C}_6$ reacting with 1 M $\text{LiAsF}_6/\text{PC-EC}$ electrolyte. This series of ARC samples consisted of 1.7 g carbon and 2.0 g electrolyte hermetically sealed in a 5.2 g steel can. The $\text{Li}_{1/2}\text{C}_6$ was prepared by equilibrating Conoco XP coke pellets at 0.02 V vs. lithium. For comparison the exotherm for the 25 cycle Li/MnO_2 cell from Fig. 2 is included.

Table 1
Details of ARC samples compared in Fig. 3

Sample description	Total lithium (mAh)	Heat capacity ($\text{Cal}/^\circ\text{C}$)	Start temperature ($^\circ\text{C}$)
Li_xC_6 , 3.5 m^2/g	444	1.69	120
Li_xC_6 , 6.4 m^2/g	442	1.83	120
Li_xC_6 , 19 m^2/g	560	1.99	120
Li/MnO_2 cell *	1200	2.79	100

* After 25 cycles at C/20.

lithium metal anodes. Table 1 gives details including the total amount of lithium and the heat capacity for each of these samples. Although the Li/MnO_2 cell has a larger heat capacity and starts from a lower temperature than the Li_xC_6 samples, its self-heating rate is higher than all but the highest surface area Li_xC_6 sample. By selecting a low surface area carbon anode material we can ensure that the anode is insensitive to thermal abuse and remains so as the cell is cycled.

This has been verified by testing the thermal stability of prototype lithium-ion cells. Fig. 4 shows 140 °C hot-box data for fully charged $\text{LiCoO}_2/\text{coke}$ 4/3A-size cells (nominal capacity=800 mAh) after 2 and 100 cycles. Unlike the lithium metal anode cells shown in Fig. 1, the temperature overshoot diminishes as these cells are cycled. Similar trends have been reported elsewhere [1]. The improved thermal stability after many cycles may be due to the gradual passivation of the carbon surface by electrolyte decomposition products which is believed to be responsible for gradual capacity loss [6].

Unlike the lithium metal anode which becomes less stable as cells are cycled, the carbon anode is most

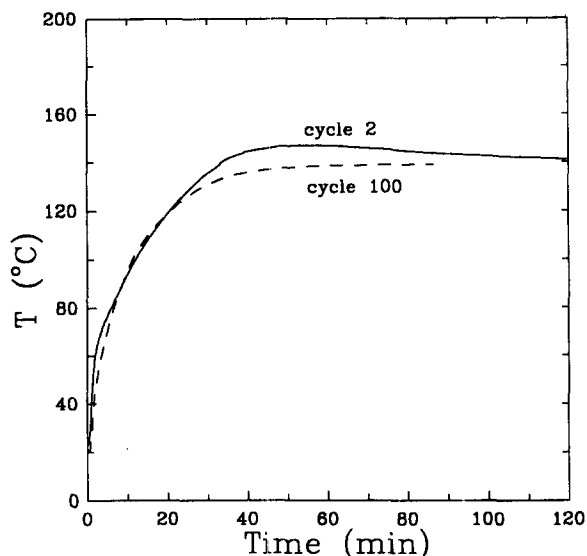


Fig. 4. Temperature response curves of cycled $\text{LiCoO}_2/\text{coke}$ 4/3A-size cells containing 1 M $\text{LiPF}_6/\text{PC-DEC}$ electrolyte subjected to 140°C hot-box test. Nominal cell capacity = 800 mAh. The number of cycles completed prior to the hot-box test is indicated on the graph.

sensitive when cells are fresh. As long as we stay within the bounds of normal operating conditions factors such as cycling temperature, depth-of-discharge and discharge rate are not expected to have a significant impact on the safety of lithium-ion cells. This makes the task of confirming the safety of lithium-ion cells manageable because unlike cells with lithium metal anodes, brand new cells are most sensitive to abuse.

Although anode morphology is the most important factor determining the thermal stability of the anode, other factors also play a role. Fig. 5 shows how the state-of-charge of the carbon anode affects the reaction rate. A high surface area sample ($19\text{ m}^2/\text{g}$) was chosen to better illustrate the effect. Conoco XP pellets were equilibrated at successively lower voltages (0.3 to 0.001 V) versus lithium metal in 1 M $\text{LiAsF}_6/\text{PC-EC}$ electrolyte, and then reacted with this same electrolyte starting from 120°C . The carbon equilibrated at lower voltages is more reactive, as it to be expected since (i) the concentration of lithium in Li_xC_6 and (ii) the heat of reaction both increase as the anode approaches lithium potential. Note that the curves for samples equilibrated at higher voltages (lower x values) exhibit a downward trend at higher temperatures, suggesting that eventually the reaction rate is being limited by lithium depletion at the surface of the carbon. Depletion occurs even sooner when a lower surface area carbon is used (see Fig. 3).

The choice of solvents also affects the reaction rate. Fig. 6 shows ARC exotherms for a series of identically prepared coke samples except that different electrolyte cosolvents were used: 1 M $\text{LiPF}_6/\text{PC-R}$ where $\text{R} = \text{EC}$, dimethoxyethane (DME), diethyl carbonate (DEC) or

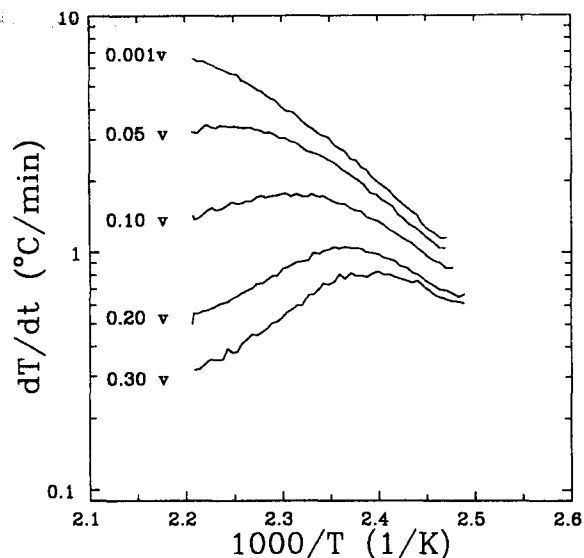


Fig. 5. Effect of state-of-charge on the ARC exotherm of high surface area ($19\text{ m}^2/\text{g}$) Conoco XP coke reacting with 1 M $\text{LiAsF}_6/\text{PC-EC}$ electrolyte. These Li_xC_6 samples were prepared by equilibrating coke pellets at various voltages vs. lithium, as specified on the graph. This series of ARC samples consisted of 0.85 g of carbon and 1.3 g of electrolyte hermetically sealed in a 4.0 g steel can.

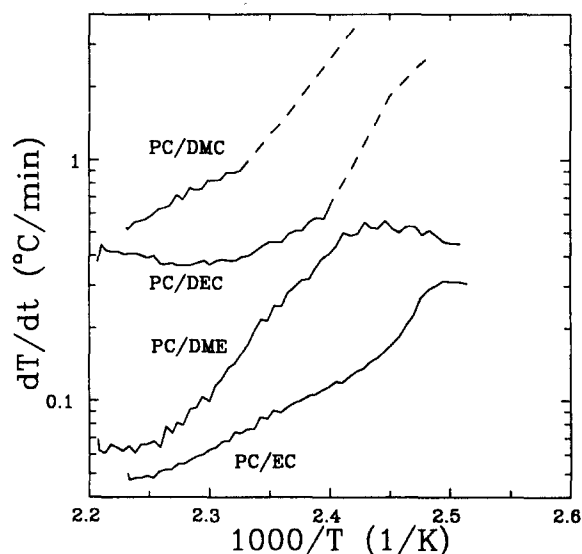


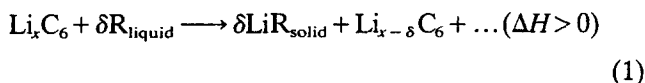
Fig. 6. Effect of electrolyte solvent on ARC exotherms of identical Li_xC_6 ($x = 0.55$) samples reacting with 1 M $\text{LiPF}_6/\text{PC-R}$ where $\text{R} = \text{EC}$, DME, DEC or DMC. This series of ARC samples consisted of 1.13 g of carbon and 1.5 g of electrolyte hermetically sealed in a 5.2 g steel can. These ARC runs well all started at 120°C . The dashed lines refer to self-heating of some samples during the initial equilibration period.

dimethyl carbonate (DMC). These Li_xC_6 samples were prepared by charging 2320 $\text{LiNiO}_2/\text{coke}$ coin cells to a fixed capacity of 202 mAh per gram of coke as described by Wainwright [7], then recovering the charged anode pellets to prepare the ARC samples. All of the ARC runs were started at 120°C but the samples containing DEC and DMC cosolvents self-

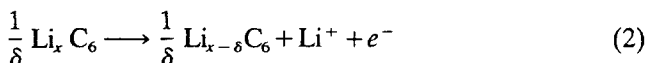
heated rapidly during the initial 10 min equilibration period, during which no data are collected. The self-heating rate increases in the order EC < DME < DEC < DMC. The reasons for this are not well understood but might include the relative effectiveness of passivating film, solubility of the passivating film and reactivity of solvents.

5. Reaction model

The shape of the exotherm can be qualitatively modelled as a simple heterogeneous reaction between the electrolyte solvent (R) and Li_xC_6 , where the reaction produces a passivating film on the carbon surface. We represent this by the reaction:



although this is probably oversimplified. Since lithium metal is thermodynamically unstable in aprotic solvents like PC, such a passivating film, also known as the solid electrolyte interface (SEI), has long been used to explain the fact that lithium is kinetically stable in certain solvents at moderate temperatures [8]. In essence the SEI model assumes that lithium/electrolyte reaction product(s) build up on the surface to form a film which effectively prevents further reaction, but still allows lithium ions to pass through. Eq. (1) can be separated into two half-reactions:



that show that the reaction can only proceed if electrons are transferred through the film from the carbon to the SEI/electrolyte interface, or if solvent molecules are transferred from the electrolyte to the carbon/SEI interface. Solvent molecules could penetrate the film either through imperfections, such as cracks, or if they are sufficiently mobile, through the bulk of the SEI film. Similar passivation films must form on the carbon anode. Numerous studies have been conducted on this topic but the exact nature of the SEI is still not clear [6,9,10].

We assume that the flux of electrons and/or solvent molecules through the SEI is inversely proportional to the film thickness (p) although more complicated dependencies could be envisaged. A $1/p$ (or similar) term reduces the rate of reaction as the film thickness increases, thus giving the passivating effect. Secondly, we assume that the reaction rate is proportional to the concentration of lithium at the carbon surface ($C_s(t)$). A time dependence is included explicitly because C_s does not remain constant. The lithium concentration

at the surface of a carbon particle is determined by the rate at which lithium diffuses from the interior of the particle to replenish what is consumed by the reaction at the surface. Thus the lithium flux (J) reacting at the surface of a carbon particle is given by:

$$J = \frac{AC_s(t)}{p} \exp(-E/kT) \quad (4)$$

where E is an activation energy, and A is a constant. The activation energy (E) is a lumped term that may contain contributions from both the transport through the SEI and the chemical reaction.

Eq. (4) qualitatively explains the shape of ARC exotherms such as those shown in Fig. 7. Starting at moderate temperatures the growth of the SEI initially quenches the reaction through the $1/p$ term. However, as the temperature increases the exponential term begins to dominate and the reaction rate increases again until it is limited by depletion of lithium at the carbon surface. Note that the pronounced dip at the start of the exotherms depicted in Fig. 7 is only observable when ARC runs are started at sufficiently low temperatures. At higher starting temperatures the exponential term already dominates the reaction so this feature disappears.

For a distribution of spherical particles (N_r particles of radius r) the total lithium reaction rate (dn/dt) can be expressed as:

$$\frac{dn}{dt} = \sum_r 4\pi r^2 J_r N_r \quad (5)$$

where J_r is the instantaneous lithium flux at the surface of a particle of radius r .

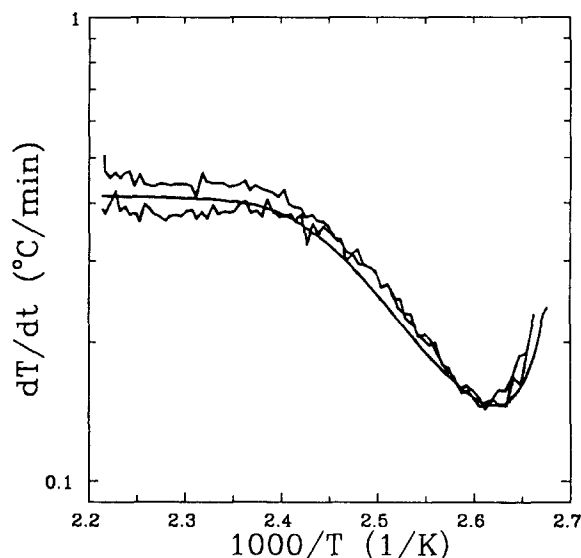


Fig. 7. Comparison of duplicate ARC exotherms for Li_xC_6 ($x=0.55$) and best fit model calculation (smooth curve). This sample consisted of 2.0 g of coke and 2.0 g of 1 M $\text{LiAsF}_6/\text{PC-EC}$ electrolyte hermetically sealed in a 5.2 g steel can. These ARC runs were started at 100 °C.

The self-heating rate is then directly proportional to the reaction rate:

$$\frac{dT}{dt} = \frac{\Delta H}{c} \frac{dn}{dt} \quad (6)$$

where ΔH is the heat of reaction, and c is the sample heat capacity.

Quantitatively fitting actual ARC data even with this simple model is difficult because detailed knowledge of the sample morphology (particle shape and size distribution) and lithium diffusion characteristics in the carbon are required to accurately model the reaction. If the unknown factors are treated as adjustable parameters it is possible to obtain a reasonably good fit using this model (see smooth curve in Fig. 7). To really test the validity of our model much more experimental work is required to obtain accurate lithium-diffusion rates, etc., so that fewer adjustable parameters are involved.

6. Conclusions

We have shown that the carbon intercalation anode is vastly superior to the lithium metal anode because it improves the thermal stability of the cell and because it provides predictable thermal stability. This is primarily due to the stable anode morphology. However, the carbon anode is nevertheless reactive and still generates heat when cells are abused. The exothermic $\text{Li}_x\text{C}_6/\text{electrolyte}$ reaction must be taken into account to ensure a safe product.

Small cells for portable electronic equipment can be tested in large numbers to statistically verify their safety, but this becomes increasingly impractical as the cell size increases. As larger lithium-ion cells (e.g., for electric vehicles) are developed it will become increasingly important to understand the exothermic reactions that occur at elevated temperatures. The ability to model such reactions and the heat flow within batteries may prove to be essential tools for the development of large-scale lithium-ion batteries.

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