

Accelerating rate calorimetry studies of the effect of binder type on the thermal stability of a lithiated mesocarbon microbead material in electrolyte

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Abstract

An Accelerating Rate Calorimeter (ARC) is used to measure the thermal behaviour of lithiated MCMB (mesocarbon microbead) electrodes, made with different binder, in electrolyte. Electrodes using PVDF, (VdF:HFP) or (VdF:CTFE) copolymer and ethylenepropylene-diene (EPD) terpolymer binders were studied. The safety results for the VdF-based binder electrodes are almost identical, within error, suggesting that the safety of Li-ion cells is not compromised or improved by changes to the binder within this group. On the other hand, the electrodes made with EPD binder, that is not plasticized by the electrolyte, appear to have the lowest self-heating rates. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The ARC (Accelerating Rate Calorimeter) has previously been used to study the thermal stability of lithium-intercalated MCMB (mesocarbon microbeads) electrodes in three different electrolytes [1]. From these results, we have concluded that the self-heating occurring at the MCMB electrode in electrolyte, at temperatures between 60 and 200°C, is due to: (1) the conversion of metastable Solid Electrolyte Interface (SEI) components to stable SEI components; and (2) the reaction of intercalated lithium, from the carbon, with electrolyte to eventually form stable SEI. The latter process is limited by the ability of the lithium to diffuse through the SEI.

The debate concerning the components of the SEI is ongoing [2–4]. XPS and FTIR results consistently show evidence for Li₂O, LiF, Li₂CO₃ and lithium semicarbonates. In addition, the binder must also be at parts of the carbon surface. As a result, the type of binder used could affect the reactivity of the lithium-intercalated carbon electrode with electrolyte.

Du Pasquier et al. [5] studied the reaction of lithium with various binders using DSC. They found that these reactions begin above 200°C. At such temperatures the thermal runaway of a fully-charged Li-ion cell is already well underway, so the *direct reaction* between Li and binder is not so important. On the other hand, the *influence of the binder on the Li/electrolyte reaction* that takes place at the carbon surface is important to study. The Li/electrolyte reaction and the decomposition of the metastable SEI layer begin near 80°C for LiPF₆-based electrolytes [1]. These reactions are primarily responsible for the onset of thermal runaway in Li-ion cells. The work to be presented here addresses the influence of the binder on the kinetics of these reactions in a qualitative, comparative manner.

A number of copolymer mixtures have been proposed as alternate binders in the last few years [6–9]. The copolymers, like vinylidene fluoride:hexafluoropropylene (VdF:HFP) or VdF:chlorotrifluoroethylene (VdF:CTFE), absorb much more electrolyte than PVDF (polyvinylidene fluoride) binder. Conversely, the ethylenepropylene-diene (EPD) binder does not absorb electrolyte. In this paper, we use an ARC to measure the strength of the reactions between lithiated MCMB electrodes, made with ho-

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Table 1
Composition, solvent and mass increase for the different binders used in this study

Binder	Composition	Solvent used for dissolution	% Mass increases in EC:DEC (1:1)
EPD	No fluorine	Cylcohexane	0
Kynar 361P	PVDF	NMP	10
Kynar 2801	88% VdF:12% HFP	Acetone	51
Solef 20810	92% VdF:8% HFP	Acetone	50
Solef 21508	85% VdF:15% HFP	Acetone	65
Solef 1012	PVDF	NMP	12
Solef 31508	85% VdF:15% CTFE	Acetone	68

mopolymer, copolymer or terpolymer binders, and electrolyte

2. Experimental

The active material is an MCMB material heated near 2800°C (Osaka Gas, Japan). The electrodes contain 7% Super S carbon black (MMM Carbon, Belgium), active material and an appropriate concentration of binder. Table 1 lists the different binders studied, their chemical compositions and the solvent the polymer was dissolved in. The electrodes made with EPD contained 2.5% by mass of EPD whereas electrodes made with any of the others

contained 7% by mass of the binder. In order to possibly link trends in the self-heating rate profiles with the amount of electrolyte absorbed by the binder, the mass gain for each binder after immersion in EC:DEC (1:1) solution for 1 day is listed in Table 1. The copolymer binders absorb much more electrolyte than the VdF-based binders.

Electrode stock fabrication, cell construction, cell cycling and ARC sample construction are described elsewhere [1]. MCMB materials were discharged in LiPF_6 EC:DEC (33:67) electrolyte to three different compositions: $\text{Li}_{0.8}\text{C}_6$ (0.0 V), $\text{Li}_{0.45}\text{C}_6$ (0.089 V) and $\text{Li}_{0.25}\text{C}_6$ (0.127 V).

The ARC samples, containing lithiated MCMB in electrolyte, were heated at 5°C/min to an initial temperature

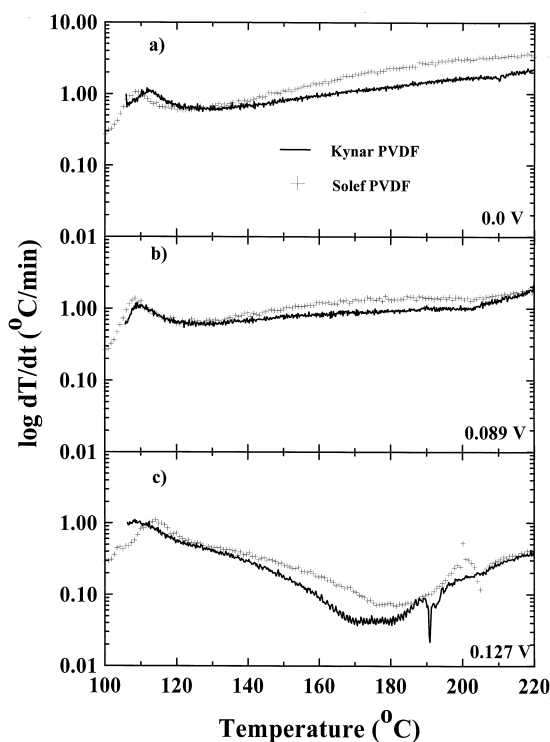


Fig. 1. Self-heating rate for lithiated MCMB electrodes, made with Kynar or Solef PVDF binder, in LiPF_6 EC:DEC (33:67) electrolyte. (a) MCMB electrodes discharged to 0.0 V, corresponding to a composition of $\text{Li}_{0.75}\text{C}_6$; (b) electrodes discharged to 0.089 V, corresponding to a composition of $\text{Li}_{0.45}\text{C}_6$; and (c) electrodes discharged to 0.127 V, corresponding to a composition of $\text{Li}_{0.25}\text{C}_6$.

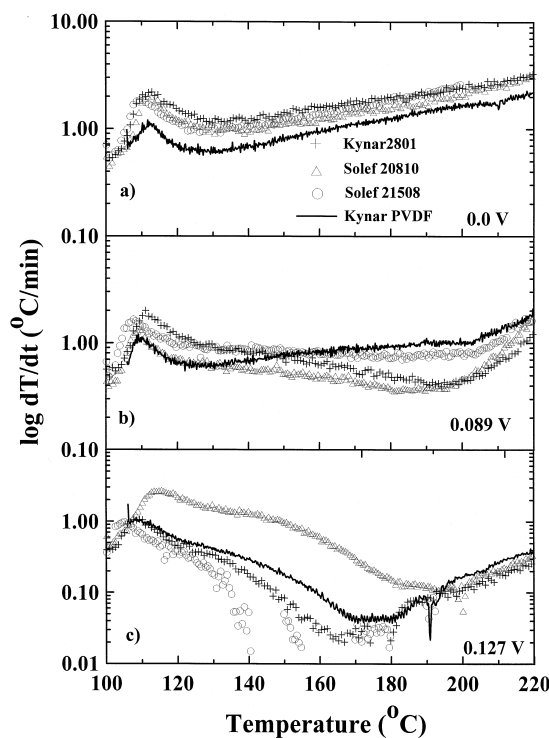


Fig. 2. Self-heating rate for the MCMB samples containing VdF:HFP copolymer binders—Kynar 2801 (88% VdF:12% HFP), Solef 21508 (85% VdF:15% HFP) and Solef 20810 (92% VdF:8% HFP). The results are compared to the electrodes made with Kynar PVDF binder. (a) lithium-intercalated MCMB electrodes with a composition of $\text{Li}_{0.75}\text{C}_6$; (b) lithium-intercalated electrodes with a composition of $\text{Li}_{0.45}\text{C}_6$; and (c) lithium-intercalated electrodes with a composition of $\text{Li}_{0.25}\text{C}_6$.

of 100°C. Lithium-intercalated MCMB samples in LiPF₆ EC:DEC (33:67) are self-heating at this temperature [1]. The ARC proceeds directly from the heating mode to the search mode where the calorimeter matches and records any temperature increase in the sample. Self-heating greater or equal to 0.02°C/min is labeled an exotherm.

3. Results and discussion

The self-heating rate profiles measured for electrodes containing Kynar PVDF binder have previously been reported [1]. These were our initial samples, as a result, we were unsure of the heat-wait-search times to use during the measurement. The PVDF measurements were made on samples heated at 5°C/min to 100°C. The heating period was followed by a 15-min equilibration period. The lithium-intercalated MCMB samples are self-heating at 100°C, as a result during the equilibration period, the sample temperature increases to 105°C before self-heating rate results are collected.

In theory, the Kynar and Solef PVDF binders should be identical and as a result identical self-heating rate profiles are expected. The self-heating rate profiles measured for

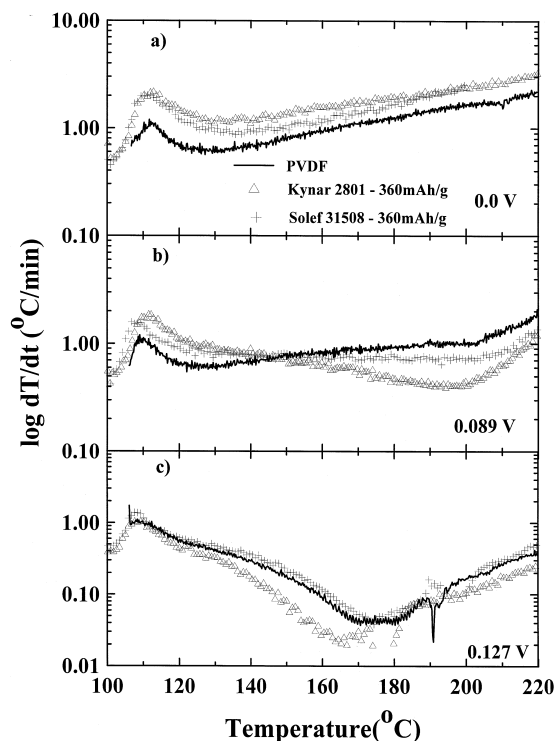


Fig. 3. Self-heating rate for MCMB electrodes containing VdF:CTFE copolymer binder—Solef 31508 (85% VdF:15% CTFE). The results are compared to the electrodes made with Kynar PVDF and to the results for electrodes made with Kynar 2801. (a) MCMB electrodes discharged to 0.0 V, corresponding to a composition of Li_{0.75}C₆; (b) electrodes discharged to 0.089 V, corresponding to a composition of Li_{0.45}C₆; and (c) electrodes discharged to 0.127 V, corresponding to a composition of Li_{0.25}C₆.

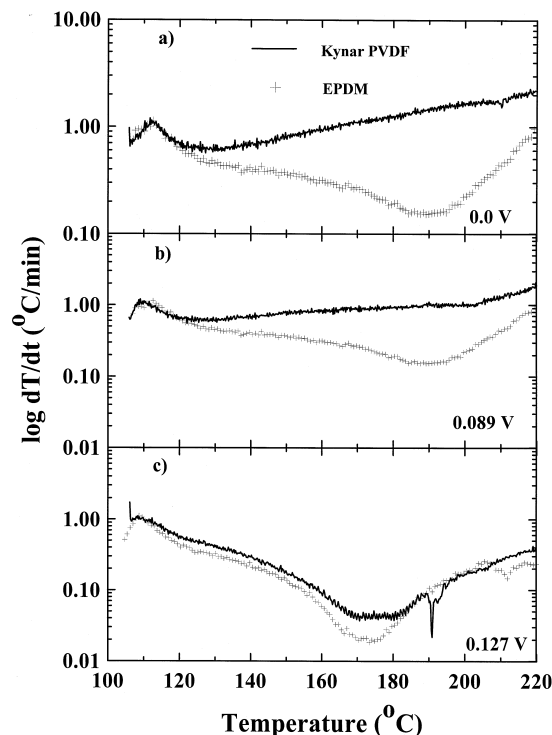


Fig. 4. Self-heating rate for MCMB electrodes containing EPDM binder compared to the Kynar PVDF binder. (a) MCMB electrodes discharged to 0.0 V, corresponding to a composition of Li_{0.75}C₆; (b) electrodes discharged to 0.089 V, corresponding to a composition of Li_{0.45}C₆; and (c) electrodes discharged to 0.127 V, corresponding to a composition of Li_{0.25}C₆.

both PVDF binders are shown in Fig. 1. The profiles for both binders are very similar. Any differences are within the variations measured for nominally identical samples presented in Richard and Dahn [1].

If the amount of electrolyte absorbed by the binder affects the self-heating rate of MCMB electrodes in electrolyte, the results for electrodes containing the copolymer VdF:HFP binders should show the effects. Fig. 2 shows the 100°C start temperature ARC results for lithium-intercalated MCMB electrodes containing the different VdF:HFP copolymers (Solef 20810, Solef 21508 and Kynar 2801) as binders. Any variations in the self-heating rate profiles shown in Fig. 2 are within the range measured for nominally identical samples presented in Richard and Dahn [1]. As a result, the effect of binder choice seems small.

The ARC results for lithium-intercalated MCMB electrodes in electrolyte containing the VdF:CTFE copolymer binder are compared to the PVDF and the Kynar 2801 results in Fig. 3. Again, the results show no dramatic variations as a result of the large plasticizability of the VdF:CTFE binder. Any variations are within the range measured for nominally identical samples presented by Richard and Dahn [1].

A final binder, one that is not plasticized by the electrolyte, was studied. The ARC results for the samples

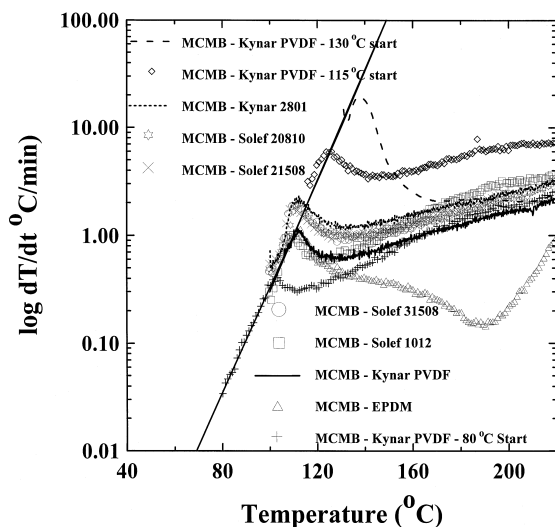


Fig. 5. Composite graph of the 0.0 V profiles for MCMB electrodes made using each of the different binders. The initial slope of the self-heating rate profiles is approximately the same for all the different binders.

containing EPD are compared to the PVDF results in Fig. 4. The peaks in the self-heating rate profiles are roughly identical, in both position and height, in all the results. The profiles are very different after the peak. In the region after the peak, all the samples made with EPDM binder consistently have a lower self-heating rate. The combination of results from Figs. 1–4 suggests the thermal behaviour is affected in a case where the binder is not plasticized at all.

The peak in the self-heating results shown in Figs. 1–4 always has roughly the same intensity and position, within variations measured for nominally identical samples [1]. In a previous work, we attributed the peak in the self heating profile of MCMB in LiPF_6 EC:DEC (33:67) to the conversion of metastable SEI components to stable SEI components. We have previously fit the initial upward slope in the self-heating profiles of lithium-intercalated MCMB electrodes in LiPF_6 EC:DEC (33:67) (heated to different initial temperatures or having different surface areas) with a single straight line [1]. The activation energy for the conversion process could then be determined. The binder has very little effect on the peak in the self-heating rate profiles, hence this same line should fit the different binder profiles presented in Figs. 1–4. Fig. 5 shows some of the self-heating results for the $\text{Li}_{0.75}\text{C}_6$ MCMB electrodes, made with the different binders, in electrolyte. Fig. 5 shows that the initial slope of all the self-heating curves can be fit with the same line, as discussed in Ref. [1].

4. Conclusions

Unlike the surface area of the active material or the electrolyte, the type of binder used in the lithium-intercalated MCMB electrode does not strongly affect its thermal stability in electrolyte. EPD binder, which is not plasticized by electrolyte, appears to give a small reduction in self-heating compared to PVDF and copolymer binders, which are plasticized. This study discerned no beneficial or deleterious effects caused by the addition of HFP or CTFE monomers to the PVDF binder. At the temperatures studied here, the binders themselves do not directly react with lithium [5]. Therefore the details of the chemistry of the binders are not important. The differences between the EPD binder and the VdF-based binders must be due to their electrolyte absorption characteristics.

The choice of binder in a commercial Li-ion cell depends on many factors, including chemical stability, ease of processing, resulting adhesion of the coating to the substrate, and so on. There may be instances where VdF-based binders containing HFP or CTFE are preferred over pure PVDF. The ARC gives qualitative and quantitative results about the reactions between Li-intercalated within the carbon electrode and electrolyte thus signaling ‘safety showstoppers’. The work presented here suggests that the safety of commercial Li-ion cells will be neither compromised nor improved by additions of HFP or CTFE to the polymer, at least at the concentrations studied here. This is a very useful result to the community.

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