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The Impact of Fluoroethylene Carbonate Additive on Charged Sodium Ion Electrodes/Electrolyte Reactivity Studied Using Accelerating Rate Calorimetry

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The effects of fluoroethylene carbonate (FEC) electrolyte additive on charged sodium ion electrode/electrolyte reactivity at elevated temperatures were investigated using accelerating rate calorimetry (ARC). The beneficial effect of FEC on cell lifetime was demonstrated using $Na_{0.97}Ca_{0.03}[Mn_{0.39}Fe_{0.31}Ni_{0.22}Zn_{0.08}]O_2$ (NCMFNZO)/hard carbon (HC) pouch cells first prior to ARC measurements. Electrodes from these pouch cells were utilized as sample materials and 1.0 M $NaPF_6$ in propylene carbonate (PC): ethyl methyl carbonate (EMC) (1:1 by vol.) was chosen as control electrolyte. Adding 2 wt% and 5 wt% FEC to the electrolyte does not significantly affect the reactivity of de-sodiated NCMFNZO compared to the control electrolyte. However, the addition of FEC obviously changed the reactivity between sodiated HC and electrolytes, especially by showing a suppression on the exothermal behavior between 160 °C and 230 °C. These results give a head to head comparison of the reactivity of FEC additive containing electrolytes with charged sodium ion electrode materials at elevated temperatures and show that the use of FEC at additive levels should not compromise the cell safety when extending cell lifetime.

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In recent years, interest in sodium-ion batteries (SIB) has increased significantly mainly due to the high abundance and relatively low price of sodium compared to lithium.[1,2] However, the insufficient lifetime of SIBs greatly impedes their wide applications as an alternative energy storage technology to support lithium-ion batteries (LIBs) on achieving carbon neutrality. The use of electrolyte additives has attracted increasing attention due to its effect on extending SIBs lifetime by improving the properties of the electrode-electrolyte interphases.[1,3] Such an interphase can be formed either on the anode side, called solid electrolyte interphase (SEI), or on the cathode side, called cathode electrolyte interphase (CEI). Both SEI and CEI lead to the decrease of side reactions between electrodes and electrolytes, thus improving cell lifetime.

The nature and dynamic evolution of both SEI and CEI are highly dependent on electrolyte composition, cell operation conditions and time. Although a full understanding of both SEI and CEI is elusive, substantial efforts have been devoted to illustrating their chemical compositions, morphology, and properties for SIBs. Leveraging density functional theory (DFT) calculation, Liu et al.[4] revealed that the priority of one-electron reduction to produce organic SEI species was in the order of vinylene carbonate (VC) > propylene carbonate (PC) > ethylene carbonate (EC). Na_2CO_3 component could also be generated by a two-electron reduction in the order of EC > PC > VC. Using Fourier transform infrared (FTIR) spectroscopy, Eshetu et al.[5] realized the presence of sodium double alkyl carbonate (NEDC) as SEI composition on the surface of hard carbon (HC) anode, which could be caused by the one electron reduction of EC. Na_2CO_3 was also detected when linear carbonates (e.g. diethyl carbonate (DEC), dimethyl carbonate (DMC)) were used as co-solvents. In addition to NEDC, Pan et al.[6] found NaF in the SEI of HC after 25 cycles in the electrolyte of 1 M $NaPF_6$ in EC/DEC. Komaba et al.[7] reported a HC SEI consisting of Na_2CO_3, $ROCO_2Na$, CH_2-, and $-CO-O-$ ester linkages using X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS). According to the report from Lee et al.,[8] DMC could be continuously decomposed without CEI protection when $Na_4Fe_3(PO_4)_2(P_2O_7)$ stayed at a high voltage. Yun et al.[9] studied the CEI of $Na_3V_2(PO_4)_2F_3$ cathode and reported the composition of R–COOH and $NaPO_2F_2$ when tuning the hydrolysis of $NaPF_6$. By artificially building a CEI of Al_2O_3 on the surface of P2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ using atomic layer deposition (ALD), Alvarado et al.[10] extended the cell lifetime in the electrolyte of 1 M $NaPF_6$ in PC.

Fluoroethylene carbonate (FEC) is one of the most commonly used electrolyte additives in SIBs and is believed to be an effective SEI and CEI-forming additive to improve cell lifetime.[11] Fondard et al.[12] carefully studied the SEI composition of HC after 135 cycles with 3% FEC and 1 M $NaPF_6$ in EC/DMC (1/1) using XPS and found that NEDC and NaF were the main compositions. Dahbi et al.[13] extended the capacity retention of HC/Na cells by using FEC additive in the electrolyte of 1 M $NaPF_6$ in PC. By using XPS and TOF-SIMS, they showed that the outermost SEI compositions of HC were enriched with inorganic species (e.g. NaF), which could be due to the decomposition of FEC. With the addition of 5 vol% FEC, Liu et al.[14] exhibited a considerable long-term cycling performance up to 1500 cycles with 84% capacity retention at 200 mA g^{-1} for HC/Na cells in the electrolyte of $NaClO_4$ in trimethyl phosphate (TMP). Wang et al.[15] proved the FEC derived SEI was able to largely restrain the interphasial electron leakage. Lee et al.[8] demonstrated an excellent capacity retention of 97.5% after 300 cycles at C/2 for $Na_4Fe_3(PO_4)_2(P_2O_7)$/Na cells when FEC was used as additive in the electrolyte of 0.5 M $NaClO_4$ in EC/PC/DEC (5/3/2, by vol.). This was ascribed to the formation of NaF containing CEI with a function of preventing undesirable decomposition of linear carbonates. Nimkar et al.[16] reported an improved capacity retention of 95% for $Na_{0.44}MnO_2$/Na cells after 250 cycles

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with 1 M $NaPF_6$ in PC + 2%FEC. A richer CEI chemistry was ascribed to the possibility of HF elimination from FEC, forming highly reactive species with double bonds as feedstocks. Li et al.[17] also demonstrated a capacity retention of 93% after 500 cycles at 1 C for $Na_{0.67}Mn_{0.8}Cu_{0.1}Mg_{0.1}O_2$/Na cells in the electrolyte of 1 M $NaPF_6$ in EC/DMC (1/1 by vol.) + 1% FEC. The dissolution of transition metal ions (Cu, Mn, Mg) was reported to be highly limited by the CEI formed from FEC.

Electrolyte additives are able to modify both SEI and CEI through affecting the reactions between the charged electrodes and the electrolytes. Such reactions at highly elevated temperatures could exhibit exothermal behavior and cause safety-related issues in Na-ion cells in rare cases. Accelerating rate calorimetry (ARC) is a useful method to characterize the reactivity of charged electrode materials with electrolytes at materials level and elevated temperature conditions, which providing qualitative predictions about the cell safety performance subjected to thermal abuse.[18–21] Previous work showed the advantage of using ARC on characterizing the effect of electrolyte additives on LIB safety.[22,23] Therefore, it is important to use ARC to test the impact of common electrolyte additives with different amounts on the reactivity of charged electrode materials with electrolytes for SIB chemistries. In this work, the reactivity of sodiated HC or de-sodiated $Na_{0.97}Ca_{0.03}[Mn_{0.39}Fe_{0.31}Ni_{0.22}Zn_{0.08}]O_2$ (NCMFNZO)[24] with electrolytes containing different amounts of FEC additive was studied using ARC. These results are expected to provide a qualitative guidance on developing safer SIBs for scientists and engineers in this field. In parallel, the effect of FEC additive on cell electrochemical performance was demonstrated using jelly rolls containing NCMFNZO/HC pouch cells with a capacity of ~210 mAh.

Experimental

Electrode and electrolyte preparation.—Machine-made 210 mAh NCMFNZO/HC pouch cells, without electrolyte, were obtained from Lifun Technology (Zhuzhou, Hunan, China). The cathode is made up of 95 wt% NCMFNZO active material, 3 wt% carbonblack, and 2 wt% polyvinylidene fluoride (PVDF) binder. The anode is made of 95 wt% HC active material and 5 wt% binder. The areal loadings of cathode and anode are 16 $mg\ cm^{-2}$ and 9.47 $mg\ cm^{-2}$, respectively. The current collector for both electrodes was made of aluminum foil. The active electrode area is ~99.58 cm^2. The separator is polyethylene with a ceramic coating layer on the side facing cathode. 1 m $NaPF_6$ (>98.0%, TCI) in PC ($H_2O < 20$ ppm, Gotion): ethyl methyl carbonate (EMC, $H_2O < 20$ ppm, Gotion) (1:1 by vol.) was used as a control electrolyte in this work. Electrolytes with additives were fabricated by dissolving FEC ($H_2O < 20$ ppm, Gotion) into the control electrolyte according to different ratios.

Electrochemical measurements.—The dry pouch cells were filled with 1 g of electrolyte and vacuum-sealed using a compact vacuum sealer (MSK-115A-111, MTI Cor.) under −90 kPa gauge pressure with140 °C as a sealing temperature and 5 s sealing time inside an Ar-filled glove box. During the formation step, all the cells were transferred to 40 ± 0.1 °C temperature-controlled chambers (Neware Battery Testing System, Shenzhen, China) and rested for 3 h before charging to 4 V with C/20. The cells were then discharged to 3.1 V with C/20 for degas step. To prepare high state-of-charge electrodes for the following ARC characterizations, the cells were discharged to 1.5 V and charged back to 4 V using C/20, then were held at 4 V till the current reached C/200. long-term cycling testing was performed at 40 °C between 1.5 V and 4 V at a rate of C/3 in constant current constant voltage (CCCV) mode on charge with a C/10 cut-off current, and a rate of C/3 in CC mode on discharge. A special cycle was performed every 50 cycles at C/20 to investigate the low-rate capacity loss. To study the specific capacity of active materials, coin cells were prepared. To obtain the electrodes for coin cells, dry pouch cells were carefully cut open and the jelly roll was extracted and unrolled to separate the cathode and anode. To obtain single side coated electrodes, N-methyl pyrrolidone (NMP) was used to remove electrode materials from the current collector inside the glovebox. Single-sided coin cell sized (0.95 cm^2) cathode and anode were punched out, respectively. 2032 coin cells were fabricated using these electrodes coupled with Na metal electrode. One piece of polypropylene blown micro fiber (BMF) and one piece of 16 μm trilayer membrane with polypropylene-polyethylene-polypropylene (PP-PE-PP) configuration (Celgard) were used as the separator. ~100 μl of control electrolyte was used. Coin cells were tested at 25 ± 0.1 °C in a temperature-controlled chambers (Neware Battery Testing System, Shenzhen, China). NCMFNZO/Na and HC/Na cells were cycled at C/20 with voltage ranges of 2–4 V and 0.005–2 V, respectively.

Accelerating rate calorimetry (ARC) measurements.—To obtain charged electrodes as ARC samples, 4 V pouch cells were transferred into an Ar-filled glovebox and cut open. Double-sided coin cell sized (1.33 cm^2) de-sodiated cathode and sodiated anode electrodes were punched out, rinsed twice by DMC, and dried out under vacuum. Every piece of electrode has a capacity of ~5.3 mAh, when a total capacity of 200 mAh and a total area of 99.58 cm^2 are used for calculation. One piece of electrode was sealed with 25 mg electrolyte into a stainless-steel tube using tungsten inert gas welding inside an Ar-filled glovebox.[18,25] The sample was then hooked on the thermocouple of an accelerating rate calorimeter (MMC 274 Nexus, NETZSCH) for testing. Samples were weighed before and after ARC experiments to verify that no loss of electrolyte had occurred. The ARC testing was tracked under adiabatic conditions when the sample self-heating rate (SHR) exceeded 0.03 °C min^{-1}. The ARC data was collected in the temperature range of 50 °C −300 °C for both cathode and anode samples. Experiments were set to be automatically stopped at either above 320 °C or when the SHR exceeded 10 °C min^{-1}.

Materials characterization.—X-ray diffraction (XRD) patterns were collected using a PANalytical's X'Pert PRO Materials Research Diffractometer (Cu-Kα 1 radiation 10 – 70° 2θ range). Rietveld refinement was performed to determine crystal structure and lattice parameters using the GSAS-II software. The scanning electron microscope (SEM) images of the electrodes taken from the pouch cell were obtained using JEOL JSM-6480 SEM with an accelerating voltage of 20 kV. SEM investigation in combination with image analysis (imageJ Software) was used for morphological inspection and estimation of particle size distribution.

Results and Discussion

The structure and morphology of cathode and anode electrode materials were investigated by XRD and SEM (Fig. 1), respectively. These electrodes were obtained from fresh dry pouch cells. HC anode demonstrates a spherical morphology with a mean diameter of 5.63 μm and standard deviation of $\sigma = 2.01$ μm (Figs. 1A and S1). The typical XRD pattern of HC (Fig. 1B) was confirmed with a broad (002) peak near ~25° and (100) peak near 42°.[26] The peak at ~15° could be resulted from the binder. Al (220) peak is from the Al current collector. According to SEM, NCMFNZO cathode consists of flat particles with a wide range of diameter distribution. (Fig. 1C and S1). The XRD pattern and its refinement of NCMFNZO demonstrates its high crystallinity (Fig. 1D and Table S1). Its hexagonal layered O3 structure with R-3m space group and lattice constants of a = b = 2.96944 Å, c = 16.07944 Å is consistent with the results of the previous report on the same cathode material.[24] The minor peak at ~26.7° can be ascribed to the graphite added to the cathode electrode (Fig. 1D). The surface area of HC and NCMFNZO is 3 m^2/g and 0.7 m^2/g, respectively.

To obtain the typical voltage vs capacity profile for HC anode and NCMFNZO cathode used here, Na metal electrode and the control electrolyte were used to assemble half-cells with them,

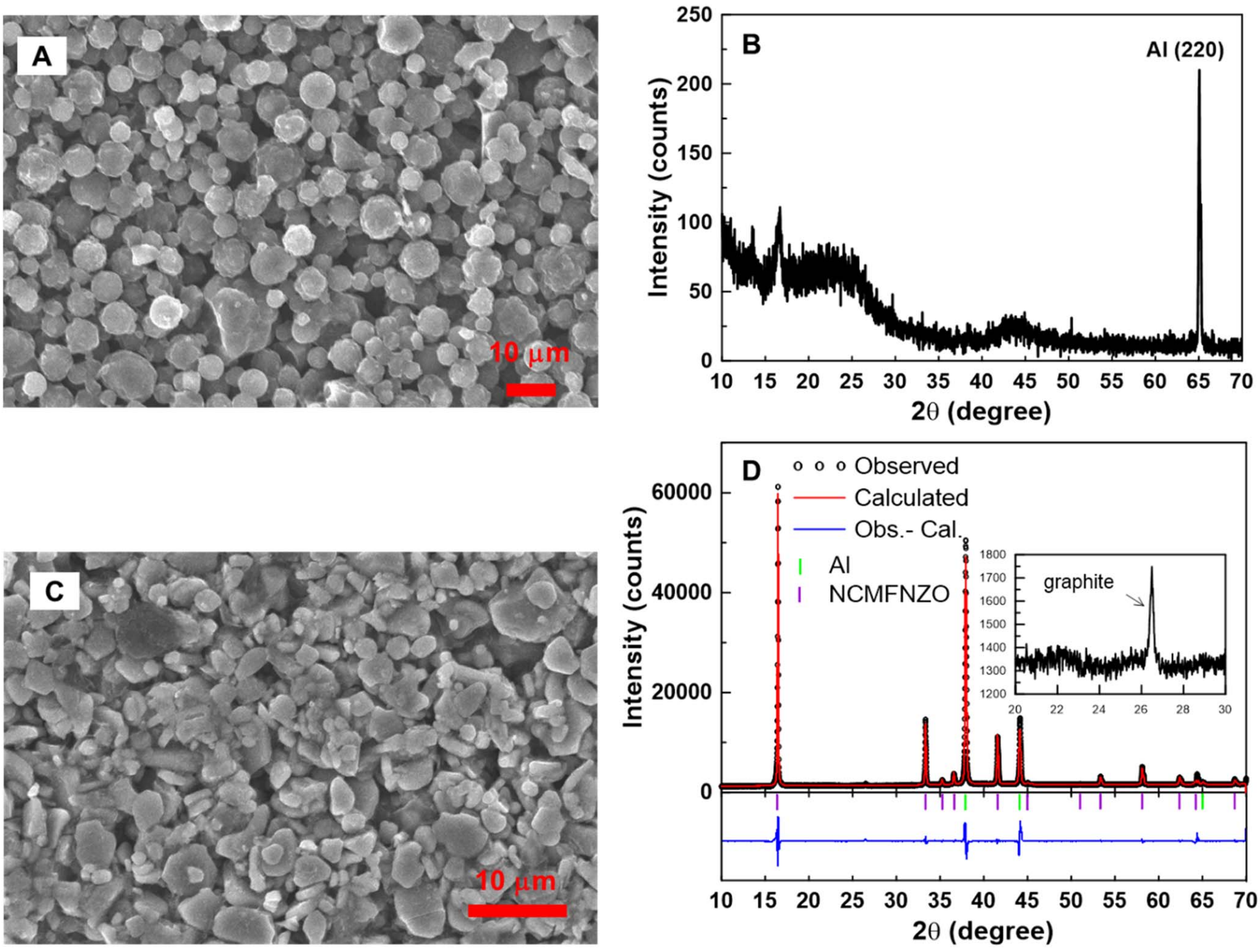

Figure 1. Electrode materials characterization. SEM images (A, C) and XRD pattern (B, D) of the HC anode (A, B) and NCMFNZO cathode (C, D).

respectively. Both NCMFNZO and HC electrodes were punched from the fresh dry pouch cells. A typical sloped voltage profile was obtained from NCMFNZO/Na half cells between 2 and 4 V (Fig. 2A) and provides a specific charge capacity of ~160 mAh g^{-1}. The irreversible capacity loss during the first cycle has been demonstrated to be decreased when electrolyte compositions were optimized.[13,27] Meanwhile, a specific discharge capacity of 300 mAh g^{-1} during the first cycle was observed with a typical sloped region and a plateau region between 0.005 and 2 V for HC/Na half cells (Fig. 2B).

Although FEC as an electrolyte additive has been widely reported to improve the electrochemical performance of SIBs, most of the testing vehicles in the literature were coin cells or even coupled with Na metal anode as half-cells. To test the effect of FEC additive on cell lifetime in a more practical way, NCMFNZO/HC pouch cells with 210 mAh balanced up to 4 V (Fig. S2) were used in this work. Concentrations of 2 and 5 wt% were selected for FEC at electrolyte additive level. Prior to long-term cycling, the first cycle Coulombic efficiency (CE) during formation at 40 °C with C/20 is 82.49%, 85.80%, and 84.92% for control electrolyte, 2 wt% FEC, and 5 wt% FEC, respectively. Although the addition of FEC improves the first cycle CE with better SEI and CEI, the increase of FEC up to 5 wt% does not dramatically affect the first cycle CE. This suggests a major consumption of electrolyte during the formation step. The data of normalized discharge capacity (Fig. 2C) and voltage polarization (Fig. 2D) vs cycle number for these pouch cells were collected during long-term cycling at 40 °C between 1.5 and 4.0 V using CCCV mode (C/3, C/10). A slow rate cycling using C/20 was performed every 50 cycles to investigate the capacity loss caused by Na inventory loss. In Fig. 2C, all the discharge capacity was normalized based on the discharge capacity of the first cycle using C/3. The cell with control electrolyte loses 15% capacity after 200 cycles. With the addition of both 2 and 5 wt% FEC additive, the cell capacity retention is obviously improved. 5 wt% FEC shows better results compared to 2 wt% FEC, especially when a higher capacity retention is observed during the "C/20 checking" cycling. This suggests more FEC could be needed to repair SEI or CEI to prevent further side reactions between electrolytes and electrodes. The delta V (Fig. 2D) is the difference between the average charge and the average discharge voltage, which indicates the polarization growth during cycling. The addition of FEC additive suppresses the polarization growth compared to the control electrolyte, which could partially contribute to the cell lifetime extension. Detailed analysis of cell failure mechanisms will be discussed in our following work.

ARC experiment was then performed to characterize the effect of FEC additive on the thermal stability of sodiated HC and de-sodiated NCMFNZO. Figure 3 shows the self-heating rate (SHR) vs temperature for 5.3 mAh sodiated HC heated with 25 mg electrolyte between 50 and 300 °C. The duplicated results are also given to demonstrate the repeatability of these experiments. Taking a closer look at the onset temperature of exothermal behavior, the addition of FEC causes an earlier onset temperature of 80 °C compared to that of control electrolyte (i.e. 90 °C). This is consistent with previous report about the effect of FEC on the thermal reactions between lithiated graphite and electrolytes.[23] Additionally, the use of 5 wt% FEC shows an exothermic peak with limited SHR (<0.2 °C min^{-1})

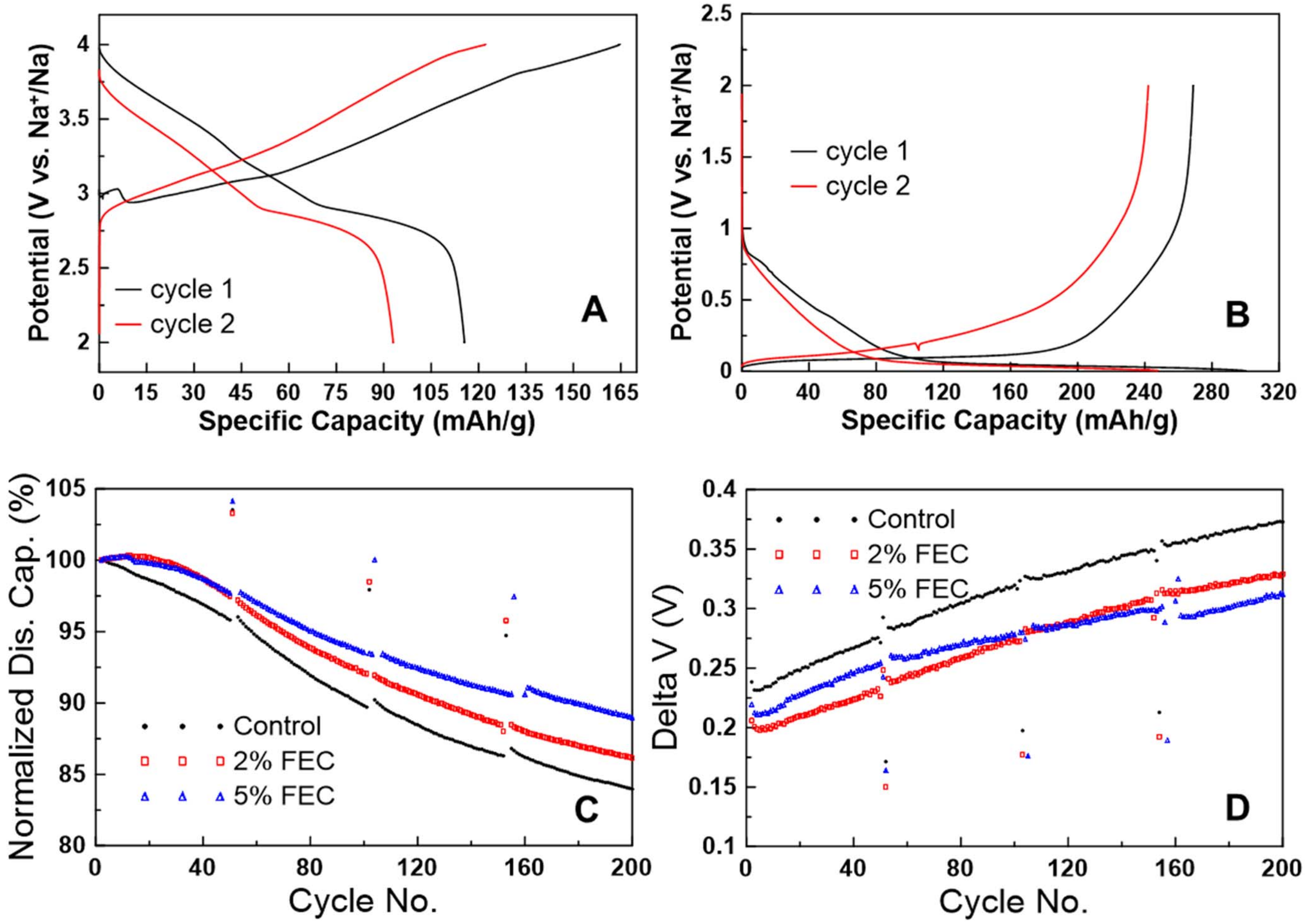

Figure 2. Electrochemical performance. Voltage vs specific capacity reference curves of NCMFNZO (A) and HC electrode (B) cycling in sodium metal half cells at C/20 and 25 °C with control electrolyte (i.e. 1 m $NaPF_6$ in PC:EMC (1:1 by vol.)). Normalized discharge capacity (C) and voltage polarization vs cycle number (D) for Na-ion pouch cells cycling between 1.5 and 4.0 V at C/3 and 40 °C with different electrolytes as labeled. A cycle of C/20 was performed every 50 cycles.

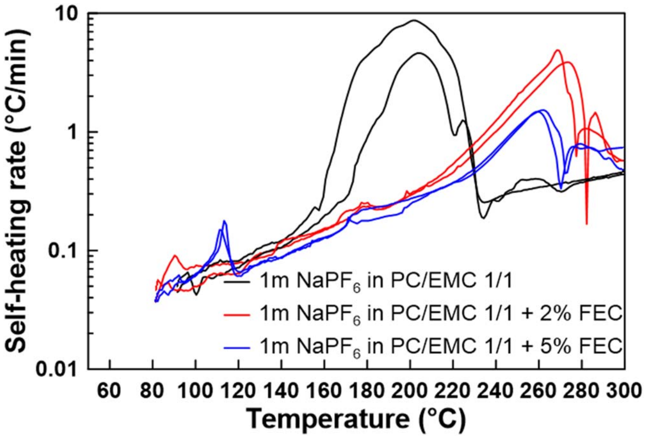

Figure 3. SHR vs temperature for sodiated HC reacting with 1 m $NaPF_6$ in PC/EMC (1/1 by vol.) with 2 wt% (red curve) and 5 wt% (blue curve) FEC compared with the control electrolyte (black curve).

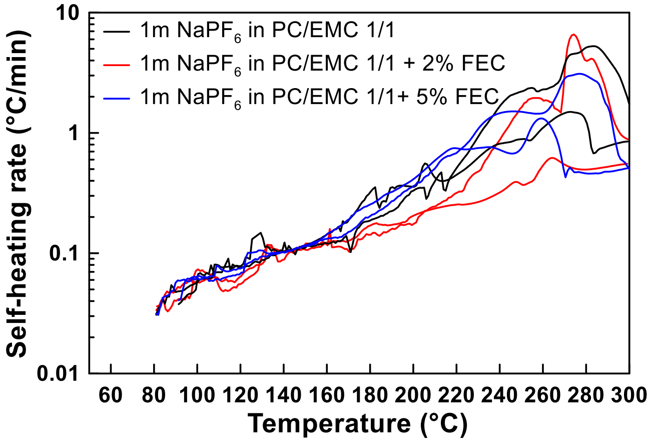

Figure 4. SHR vs temperature for de-sodiated NCMFNZO reacting with 1 m $NaPF_6$ in PC/EMC (1/1 by vol.) with 2 wt% (red curve) and 5 wt% (blue curve) FEC compared with the control electrolyte (black curve).

between 100 and 120 °C. Surprisingly, the use of FEC at an additive level dramatically decreases SHR between 160 and 220 °C, which could be due to the formation of a thermally robust SEI.

Figure 4 shows the SHR versus temperature results for 5.3 mAh de-sodiated NCMFNZO heated with 25 mg electrolytes between 50 and 300 °C. Unlike sodiated HC, FEC additive does not have a strong impact on the SHR versus temperature of charged NCMFNZO compared to the control electrolyte. However, there are still some differences between the three electrolytes. Here, the addition of FEC additive also causes an earlier onset temperature of 80 °C compared to that of control electrolyte (90 °C). 2 wt% FEC slightly decreases the SHR between 180 and 230 °C while 5 wt%

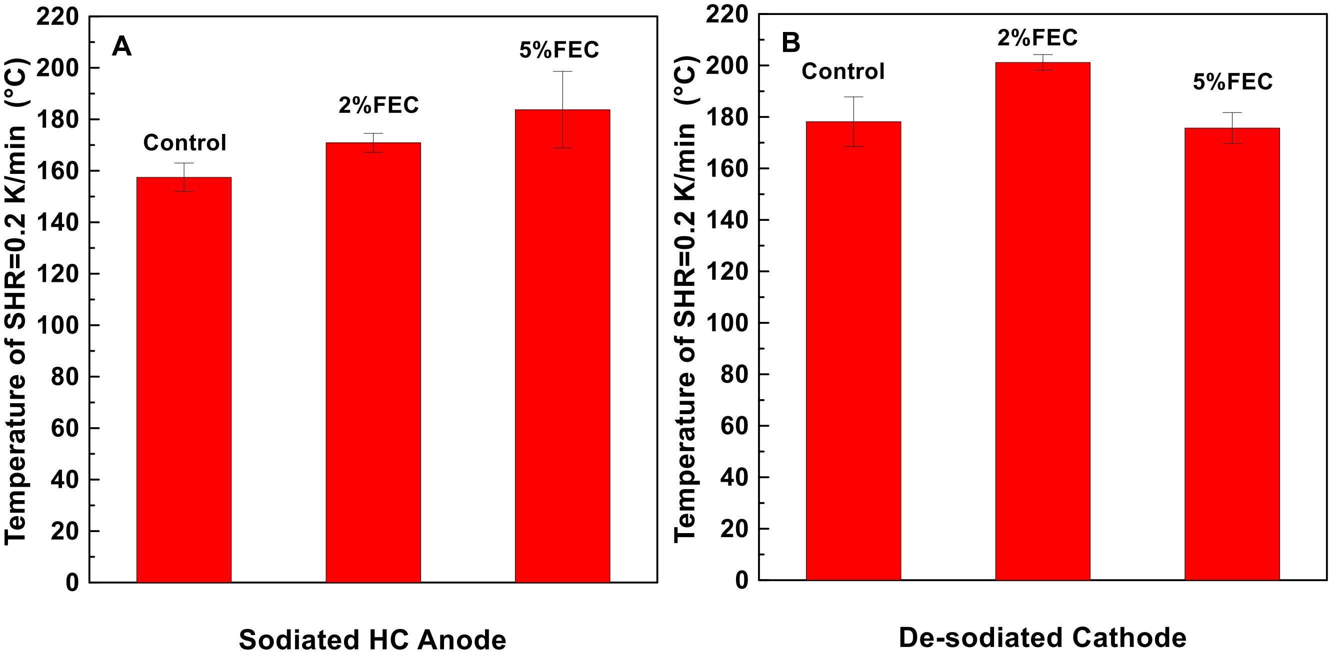

Figure 5. Temperature of the system when the SHR reaches 0.2 °C/min for electrolytes reacting with sodiated HC (A) or de-sodiated NCMFNZO (B) at elevated temperatures.

FEC shows very similar performance compared to the control electrolyte during the whole temperature range.

Figure 5 shows the temperature where the SHR first reaches 0.2 °C $\min^{-1}$ plotted versus electrolyte compositions for sodiated HC (Fig. 5A) and de-sodiated NCMFNZO (Fig. 5B), respectively. Two results were plotted for each data point and the error bar represents the difference between two measurements. According to the previous report from Wang et al.,[18] a SHR of 0.2 °C $\min^{-1}$ (in these ARC tube samples) suggests the temperature where electrode-electrolyte reactions will result in thermal runaway in 18650-size Li-ion cells. Based on such an estimation, the use of FEC additive at both 2 and 5 wt% levels are able to delay the temperature approaching 0.2 °C/min for the reactions between sodiated HC and electrolytes (Fig. 5A). In terms of the reactions between de-sodiated NCMFNZO and electrolytes, the addition of 2 wt% FEC shows a higher onset temperature (i.e. ~200 °C) when reaching 0.2 °C $\min^{-1}$ (Fig. 5B). As a note passing by, further investigations at cell level are required to verify the onset temperatures of thermal runaway when FEC additives are used.

Conclusions

In this work, the effect of two different concentrations (2 and 5 wt%) of FEC additive on extending cell lifetime was demonstrated in NCMFNZO/HC pouch cells. Addition of 5 wt% FEC resulted in a very stable capacity retention of ~90% after 200 cycles up to 4 V at 40 °C. These results are consistent with reported beneficial effects of FEC additive on SIB chemistries.

The effects of FEC additive on the reactivity of sodiated HC or de-sodiated NCMFNZO with electrolytes were carefully studied using ARC. The addition of 2 and 5 wt% FEC lead to a lower temperature exotherm (~80 °C) compared to the control sample (~90 °C) between sodiated HC and electrolytes. Especially, the addition of 5 wt% FEC results in a minor exothermic peak at ~110 °C. However, the SHR is dramatically suppressed by the addition of 2 and 5 wt% FEC between 160 and 220 °C. By contrast, the addition of FEC at an additive level (up to 5 wt%) has no obvious effect on the reactivity of de-sodiated NCMFNZO with electrolyte at elevated temperatures. The addition of 2 wt% FEC showed a decreased SHR in the temperature range of 180 °C−220 °C compared to the control electrolyte. Comparing the temperature of SHR = 0.2 °C/min for both HC and NCMFNZO, the addition of 2 and 5 wt% FEC should not cause an earlier onset temperature of thermal runaway in a large format cell according to the previous report.

This research provides valuable insights into optimizing electrolyte additives amount for enhancing the thermal stability of cathode and anode materials in SIBs, which can contribute to the development of safer and more efficient energy storage systems. Further investigations are needed to understand the underlying mechanisms responsible for the observed effects and to explore other additives to improve the thermal stability of such systems. It would be ideal if the use of electrolyte additives can simultaneously improve the electrochemical performance and suppress the reactions between charged electrodes and electrolytes at elevated temperatures in the future development of SIB electrolytes.

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