

Very Important Paper

Comprehensive Insights into the Reactivity of Electrolytes Based on Sodium Ions

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We report a systematic investigation of Na-based electrolytes that comprise various NaX [X = hexafluorophosphate (PF₆), perchlorate (ClO₄), bis(trifluoromethanesulfonyl)imide (TFSI), fluorosulfonyl-(trifluoromethanesulfonyl)imide (FTSI), and bis-(fluorosulfonyl)imide (FSI)] salts and solvent mixtures [ethylene carbonate (EC)/dimethyl carbonate (DMC), EC/diethyl carbonate (DEC), and EC/propylene carbonate (PC)] with respect to the Al current collector stability, formation of soluble degradation compounds, reactivity towards sodiated hard carbon (Na_x-HC), and solid–electrolyte interphase (SEI) layer formation. Cyclic voltammetry demonstrates that the stability of Al is

Introduction

Amongst post-lithium energy storage devices, the sodium ion battery (NIB) appears to be the most appealing and viable technology.^[1-6] Unlike Li, Na mineral deposits are unlimited, attainable at low cost, and distributed evenly. If the practical deployment of NIBs could be realized, there will be approximately a three-orders of magnitude relaxation in the constraints on resources (Table 1), accompanied by sustainability, improved environmental benignity, and cost reduction.^[7] Besides these salient features, NIBs also offer the advantage of using electro-

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highly influenced by the nature of the anions, solvents, and additives. GC–MS analysis reveals that the formation of SEI telltales depends on the nature of the linear alkyl carbonates and the battery chemistry (Li⁺ vs. Na⁺). FTIR spectroscopy shows that double alkyl carbonates are the main components of the SEI layer on Na_x-HC. In the presence of Na salts, EC/DMC and EC/DEC presented a higher reactivity towards Na_x-HC than EC/ PC. For a fixed solvent mixture, the onset temperature follows the sequence NaClO₄ < NaFTFSI < NaFF₆ < NaTFSI < NaFSI, and the total heat generated increases in the order NaFSI < NaTFSI < NaClO₄ < NaFTFSI.

lyte systems with a lower decomposition potential because of the higher half-reaction potential of Na than Li. The desolvation energy of Na⁺ is generally \approx 40–70 kJ mol⁻¹, lower than that of Li⁺, which implies a lower activation barrier for Na (de)insertion and thereby faster charge/discharge characteristics.^[8] However, the projected gravimetric and volumetric energy densities of NIBs are inevitably penalized by the inherent characteristics of Na, such as larger ionic radii (>30% higher than Li), atomic weight (> three times that of Li), and reduction potential (\approx 0.33 V vs. Li/Li⁺). Another anticipated challenge, even more than that of LIBs, is long-term stability because of the large size of Na, which causes a greater volume change during Na (de)insertion into host materials. Hence, to compete and go beyond the currently prevailing Li-ion technology, significant progress in the understanding of the electrode materials (both active and inactive components), electrolytes (salts, solvents, additives), and interfacial dynamics is needed urgently.

As in any electrochemical storage device, the scientific community has been active in the development of electrode materials for NIBs, however, studies that deal with Na⁺ electrolytes, interphases, and their reactivity in the vicinity of the electrified surface with (de)sodiated electrodes are few. Yet, the electrolyte should be considered equally as it is largely responsible for the lifetime and the credibly possible performances, in terms of practically accessible capacity, chemical/thermal stress (safety), rate capability, and so on. Moreover, although the experience and knowhow accumulated from LIBs could help in the development of electrolytes and the understanding of interfaces for NIBs, it does not guarantee that electrolyte solvents suitable for LIBs are also suitable for NIBs. Thus, one



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Table 1. Comparison of Li and Na.			
Characteristics	Na	Li	
ratio of reserves	1000	1	
price of carbonates [US \$ per ton]	150	5000	
cathode current collectors	$AI = 1920^{[a]}$	Cu = 6755 ^[a]	
atomic weight [g mol ⁻¹]	23	6.9	
ionic volume [Å]	4.44	1.84	
theoretical capacity [mAh g ⁻¹]	1165	3829	
voltage [V] vs. SHE ^[b]	-2.714	-3.045	
melting point [°C]	98	182	
desolvation energy [kJ mol ⁻¹] in			
DEC	148	208	
EC	152	211	
PC	158	218	
coordination preference	octahedral and prismatic	octahedral and tetrahedral	
reactivity/flammable	highly flammable	less reactive	
distribution	everywhere	70% in South America	
[a] In US\$ per ton. [b] SHE=standard hydrogen ele	ctrode.		

should not assume a simple transition of knowledge from Li⁺ to Na⁺ chemistries. For instance, although ethylene carbonate (EC)/dimethyl carbonate (DMC) and EC/diethyl carbonate (DEC) are preferred solvent mixtures in LIBs, EC/propylene carbonate (PC) has been described as the most stable and suitable for NIBs. Hence, a systematic screening, formulation, and optimization of electrolytes along with the evaluation of their interfacial properties is needed.

An understanding of the reactivity of electrolytes in the vicinity of the electrified interface is crucial as it plays a vital role to improve the irreversible capacity, interfacial resistance, cycle life, and safety of the battery system. Once again, the intriguing question here is whether the replacement of Li⁺ with Na⁺ would result in a similar solid–electrolyte interphase (SEI) layer, for example, with the same nature, composition, and reactivity, or not? Although one would initially assume similar trends, some of the peculiar characteristics, such as the larger size of Na⁺, higher solubility of Na-based SEI components/ degradation products (e.g., Na₂CO₃ vs. Li₂CO₃), lower Lewis acidity and higher reduction potential of Na⁺, could lead to a quite different SEI layer and preferential reactivity of solvent molecules.

Although their number is increasing at a fast pace, quite few reports detail the reactivity of the electrolytes and the investigation of the SEI layer in NIBs. Komaba et al.^[9] conducted a detailed investigation of surface films formed on Na_x-hard carbon (HC) by using X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) and obtained the same composition as for graphite in LIBs, that is, mainly M₂CO₃, ROCO₂M, CH₂–, and –CO–O– ester linkages (M=Li or Na). It was also reported that the SEI on HC in NIBs contains many inorganic species that are nonhomogeneous and porous in nature. Xia et al.^[10–12] studied the thermal response of Na_x-HC in the presence of various salts, such as NaPF₆ and sodium bis(trifluoromethanesulfonyl)imide (NaTFSI), and solvent mixtures by using accelerated-rate calorimetry

(ARC). In this study, a NaPF₆-based electrolyte was more reactive than NaTFSI towards sodiated HC because of the high thermal stability of NaPF₆, which results in the absence of NaF in the SEI layer. Moreover, in the presence of NaPF₆, DMC and DEC are more reactive than EC if in contact with Na_x-HC because of the preferential solvation of Na⁺ by EC, which leaves DMC and DEC in the outer sphere.

Ponrouch et al.^[13] performed an exhaustive evaluation of the thermal stability of a number of electrolytes, such as 1 M NaClO₄ in EC/DEC, PC, and EC/PC and compared them with 1 M NaPF₆/EC/PC. NaPF₆/EC/PC presented the highest onset temperature and lowest heat release (\approx 717 Jg⁻¹), comparable to fully lithiated graphite (\approx 700 Jg⁻¹, for 1 M LiPF₆ in EC/DMC). However, Zhao et al.^[14] made a comparative investigation on the reactivity of 1 M NaX (X = ClO₄ and PF₆) in EC/DMC, PC, and their Li counterparts, which demonstrated that Na-based electrolytes present a higher onset temperature and lower heat release to lead to the conclusion that NIBs could be safer battery systems than LIBs.

If we consider these previous reports, to obtain reliable data would require an in-depth and systematic investigation of Na⁺-based electrolyte systems. However, to arrive at representative conclusions, it requires data to be obtained from various electrolyte formulations that comprise of different salts and solvent blends.

In recognition of the existing gap and upcoming new opportunities with NIBs, a systematic and detailed comparative investigation on diverse Na-based electrolytes that comprise various NaX [$X = PF_{6r}$, ClO₄, TFSI, fluorosulfonyl-(trifluoromethanesulfonyl)imide (FTFSI), and bis(fluorosulfonyl)imide (FSI)] salts and solvent mixtures (EC/DMC, EC/DEC, EC/PC) was performed. Moreover, ionic liquids (ILs) were utilized for anodic AI stability comparison studies. A number of analytical tools were used, such as cyclic voltammetry (CV), differential scanning calorimetry (DSC), gas chromatography–mass spectrometry (GC–MS), and Fourier transform infrared (FTIR) spectroscopy.



The first part of this paper deals with the study of the intrinsic Al stability in the aforesaid electrolyte solutions. The second part addresses the trend in the generation of soluble degradation products that originate from the reduction of linear solvents. The last section focuses mainly on the investigation of the reactivity of sodiated HC with various Na⁺-based electrolytes by using DSC to extract information about the nature and growth of the SEI layer, the origin of SEI layer disruption, and the accompanying thermal stabilities of the various electrolyte solutions.

Results and Discussion

Comparative anodic stability of the Al current collector

One of the major benefits of NIBs is the possible use of Al foil as anode and cathode current collectors; thus, it is required that the electrolytes for NIBs have a good compatibility with it. Accordingly, CVs were collected from Al/Na cells on diverse electrolytes, namely, 1) 1 м NaX (X = PF₆, ClO₄, TFSI, FTFSI, FSI) in EC/DEC, 2) NaTFSI, NaFTFSI, and NaFSI in EC/DEC+5% NaPF₆, and 3) NaTFSI/Pyr₁₄TFSI, NaFTFSI/Pyr₁₄FTFSI, and NaFSI/ $Pyr_{14}FSI$ at 20 °C ($Pyr_{14} = N$ -butyl-*N*-methylpyrrolidinium (Figure 1 i-iv), to evaluate the anodic stability of Al. A comparison of the different salt anions in EC/DEC showed that the trend in the Al dissolution and/or anion decomposition increases in the order $NaPF_6 < NaClO_4 < NaTFSI < NaFTFSI < NaFSI$ (Figure 1 i). Imide-based electrolytes showed a hysteresis loop that was initiated at \approx 3.25, 3.31, and 3.45 V for FSI⁻, FTFSI⁻, and TFSI⁻, respectively, with a large irreversible oxidative current (e.g., up to 30 mA cm⁻² for FSI⁻) at 5.3 V vs. Na/Na⁺. However, a fast decrease in the current intensity is observed upon cycling for all electrolytes, which may be associated with the formation of a passivation layer during the first cycle, which in turn limits the reactivity of the Al working electrode (Table 2).



Figure 1. CVs measured on Al by using three-electrode Swagelok cells with i) a) NaFSI/EC/DEC, b) NaFTFSI/EC/DEC, c) NaTFSI/EC/DEC, d) NaClO₄/EC/DEC, and e) NaPF₆/EC/DEC; ii) NaTFSI in a) EC/DEC, b) EC/DEC+5% NaPF₆, and c) Pyr₁₄TFSI; iii) NaFTFSI in a) EC/DEC, b) EC/DEC+5% NaPF₆, and c) Pyr₁₄FTFSI; and iv) NaFSI in a) EC/DEC, b) EC/DEC+5% NaPF₆, and c) Pyr₁₄FTSI; and iv) NaFSI in a) EC/DEC, b) EC/DEC+5% NaPF₆, and c) Pyr₁₄FTSI.

Table 2. Maximum anodic current density $[mA cm^{-2}]$ evolution during cycling recorded at 5.3 V vs. Na/Na ⁺ .			
Electrolyte formulation	1 st	CV cycle 5 th	10 th
NaPF ₆ /EC/DEC NaClO ₄ /EC/DEC NaFSI/EC/DEC NaFSI/EC/DEC+5 % NaPF ₆ NaFSI/Pyr ₁₄ FSI NaFTFSI/EC/DEC NaFTFSI/EC/DEC+5 % NaPF ₆ NaTFSI/Pyr ₁₄ FTFSI NaTFSI/EC/DEC NaFESI/EC/DEC	5.3×10^{-2} 3.62×10^{-2} 29.5 6.34 2.07×10^{-2} 15.9 4.19×10^{-1} 1.6×10^{-2} 3.65 8.98×10^{-1}	$\begin{array}{c} 2.1 \times 10^{-2} \\ 1.61 \times 10^{-2} \\ 3.47 \\ 4.5 \\ 6.6 \times 10^{-3} \\ 3.43 \\ 2.91 \times 10^{-1} \\ 7.02 \times 10^{-3} \\ 2.88 \\ 7.8 \times 10^{-1} \end{array}$	$\begin{array}{c} 1.8 \times 10^{-2} \\ 1.38 \times 10^{-2} \\ 3.8 \times 10^{-1} \\ 1.24 \\ 5.35 \times 10^{-3} \\ 7.5 \times 10^{-1} \\ 2.2 \times 10^{-1} \\ 6.01 \times 10^{-3} \\ 2.1 \\ 6.7 \times 10^{-1} \end{array}$
NaTFSI/Pyr ₁₄ TFSI	9.38×10^{-3}	3.22×10^{-3}	1.98×10^{-3}

The stability of Al in imide-based electrolytes could be improved by the addition of a small amount of NaPF₆ (5 wt %) to the base electrolytes, which is because of the formation of fluoroaluminates (AIF₃ or AlO_xF_y) on the Al surface (Figure 1 ii–iv). This observation is in line with that reported for LiTFSI/EC/DMC,^[15] NaTFSI/PC,^[13] NaFSI/PC, and NaFSI/C₃C₁PyrFSI.^[16]

To gain an insight into the effect of solvent on the anodic stability of the Al current collector, CVs were measured in electrolyte solutions based on IL/(NaFSI, NaTFSI, and NaFTFSI). Contrary to carbonate-based electrolytes, IL-based electrolytes suppress Al corrosion, which is attributed to the formation of a protective passivation layer. Kühnel et al.^[17] showed that the solubility of Al(TFSI)₃ in LiTFSI/PC is considerably higher than that in LiTFSI/Pyr₁₄TFSI, which implies that AI(TFSI)₃ effectively serves as a passivation layer in IL-based electrolytes to prevent Al corrosion but not in organic carbonate-based electrolytes. The improvement with other IL-based electrolytes is also because of the effective protection of the assumed formation of Al(FSI)₃ and Al(FTFSI)₃, which depends on their stability and, especially, their solubility in the different electrolyte formulations. Although there is no documented data on the solubility or existence of Al(FSI)₃ and Al(FTFSI)₃ in EC/DEC, Pyr₁₄FSI, or Pyr14FTFSI, on the basis of comparison with the behavior of LiTFSI dissolved in carbonate solvents and ILs, it is reasonable to assume that the layers will be more stable in the ILs than in carbonate-based solvents.

In general, Al corrosion by NaA (A = FSI, TFSI, and FTFSI) salts can be represented schematically by a set of simple equations [Eqs. (1)-(3)]:

$$NaA \rightleftharpoons Na^+ + A^- \tag{1}$$

$$3 A^{-} + AI \rightleftharpoons AI(A)_{3} + 3 e^{-}$$
⁽²⁾

$$AI(A)_3 \rightleftharpoons 3 A^- + AI^{3+} \tag{3}$$

The equilibrium in Equation (3) determines the degree of solubility of the layers and their effectiveness. Thus, on the basis of the difference in the current density in the first CV cycle (as indicated in Figure 1 ii–iv and Table 2), it is reasonable to assume that the solubility of the layers increases in the order of Al(TFSI)₃ < Al(FTFSI)₃ < Al(FSI)₃ both in carbonate- and

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IL-based electrolytes. Beyond the first CV cycle, the combined effect of the Al-imide anion complex and the electrolyte decomposition layer could explain the attenuation of the Al dissolution with subsequent cycles.

Formation of SEI telltales and SEI investigation

Studies that deal with electrolyte degradation remain at the frontline of the research endeavors in LiBs because of the foreseeable electrolyte degradation presumably at the negative electrode. The formation of a robust SEI layer upon the initial charging can, more or less, limit the continuous degradation of electrolytes during the life of the battery system. Of the different approaches used to monitor the evolution of the SEI layer, the identification of soluble compounds formed concomitantly could help us to understand the whole electrolyte degradation process. The analysis of the ethylene biscarbonates $(1_1 \text{ and } 1'_1)$ as telltales of the SEI (Scheme 1) help us to monitor the extent of linear carbonate solvent reduction and thereby the effectiveness of the passivation layer as recently indicated by Kim et al.^[18] in the case of lithiated graphite. The question arose as to whether or not the soluble compounds detected after the first full charge (Na_x-HC) of the HC composite were the same in nature and content as in those in the case of Li salt-based electrolytes if we consider the 0.33 V potential difference between Li and Na. Hence, $1 \, \text{M}$ NaPF₆ in EC/DMC and EC/DEC electrolytes recovered from a charged cell that consists of a HC composite powder negative electrode and a NaN₃ plastic film positive electrode were analyzed by using GC-MS. The NaN₃ sacrificial salt was used to replace the metallic Na electrode known to contaminate the electrolyte with the same soluble degradation compounds. The results reveal the presence of the respective ethylene biscarbonates 1_1 and $1'_1$ (Figures 2a and b) as in the case of Li salt electrolyte, which is indicative of the same electrochemical processes. The 11/EC and $1'_{1}$ /EC peak area ratios (\approx 12.5 and 4.1%, respectively) are quite reproducible, and although the values are low, the trend in the quantity of biscarbonates $(\mathbf{1}_1 > \mathbf{1}'_1)$ generated corroborates the data obtained by the extrapolation of results obtained with a Li electrolyte at 0.33 V vs. Li/Li⁺ (Figures 2 c and d), that is, 20 and 5.1% for EC/DMC and EC/DEC, respectively.

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Figure 2. Liquid GC–MS chromatograms of 1 \mbox{M} NaPF₆ in EC/DMC and EC/ DEC electrolytes measured after the first sodiation of HC in 1 \mbox{M} NaPF₆ in a) EC/DMC and b) EC/DEC. Values provide the integrated intensity of each area of 1(')₁, compared to the integrated intensity of EC. Liquid GC–MS analysis of the electrolytes recorded during the first lithiation of graphite in c) 1 \mbox{M} LiPF₆ in EC/DMC and d) 1 \mbox{M} LiPF₆ in EC/DEC.^[18]

The main difference comes from the potential at which the soluble product is formed, that is, although the maximum production of $1'_1$ in EC/DEC appears near the lithiation stage (≤ 0.2 V vs. Li/Li⁺), in NIB, the DEC reduction is limited because of the higher half-reduction potential of Na than Li. For 1_1 , the highest quantity is generated in the 0.9–0.6 V vs. Li/Li⁺ potential range, and hence its generation is not limited by potential in the case of Na salt-based electrolytes. We infer that the nature and effectiveness of the SEI layer in both LIB and NIB could be expected to be different, which impacts the performance and safety of NIBs.

As in the case of LIBs, the evaluation of soluble compounds can also help to screen effective electrolyte additives in NIBs as



Scheme 1. Elementary steps for biscarbonate generation in linear carbonate/EC-based electrolytes.



the inhibition of the generation of the former implies the effectiveness of the additives.

Lastly, a preliminary investigation on the composition of the SEI layer formed on desodiated Na_x-HC in contact with 1 m NaPF₆ in 1) EC/DMC, 2) EC/DEC, and 3) EC/PC was performed by using FTIR spectroscopy. The FTIR spectra (Figure 3) evidence the presence of sodium double alkyl carbonate (NEDC), a 1e⁻ reduction product of EC, as the main component of the SEI layer, from the bands at $\tilde{\nu} = 1655$, 1390, 1440, 1300, 1080, and 820 cm⁻¹. Na₂CO₃ with bands at $\tilde{\nu} = 1440$ and 870 cm⁻¹ is also part of this SEI but in a lower quantity in the case of linear carbonate/EC blends.



Figure 3. FTIR spectra of fully sodiated HC after one cycle using 1 M NaPF_6 in a) EC/DMC, b) EC/DEC, and c) EC/PC.

Reactivity of Na⁺-based electrolytes

Thermal stability of neat Na salts

A stability study of a variety of Na salts was performed 1) to establish a database on the thermal properties of the salts and 2) to investigate their effect on the thermal reactivity of Na_x-HC. Notably, the thermogravimetric analysis (TGA) traces shown in Figure 4 indicated that the thermal stability of the neat salts decreases in the order NaClO₄ > NaTFSI > NaFF₆ > NaFTFSI > NaFSI. NaClO₄ outperforms all of the other salts in terms of thermal stability. However, although NaClO₄ is the most commonly used, it is restricted to academic interest because of its explosive nature in the dry state.

The thermal properties of the Na salts, which include the melting point (T_m) and decomposition temperature (T_{decom}) obtained from DSC and dynamic TGA measurements, respectively, are summarized in Table 3. Values provided in brackets refer to the corresponding Li salts. A simple comparison with the literature values indicates that Na salts are much more stable than their homologous Li salts, which is explained by their higher Magdelung energy, a parameter linked to the electrostatic energy in ionic crystals. For instance, the large difference in the thermal stability of LiPF₆ and NaPF₆ is evidenced by their decomposition, which starts at ≈ 125 and 325 °C, respectively. TGA measurements showed that LiPF₆ loses ≈ 83 % of its mass

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Figure 4. TGA profiles of neat Na salts: $NaPF_6$, $NaCIO_4$, NaTFSI, NaFTFSI, and NaFSI. For comparison, the TGA curve of the state-of-the-art salt in LIBs $LiPF_6$ is also presented.

at 250 °C, whereas NaPF₆ does not show any noticeable loss up to 300 °C. Thus, besides the gain in intrinsic safety, the higher thermal stability of NaPF₆ indicates that NIBs might perform much better than LIBs in terms of capacity retention during cycling and storage at higher temperatures. Capacity fading at elevated temperature is one of the most critical limitations of LIBs, which is mainly attributed to the thermal instability of LiPF₆-based electrolytes and leads to the generation of Lewis acids that, in turn, catalyzes parasitic cascade reactions inside the cell.

The melting points of all of the Na salts measured in this study are generally higher than those reported in literature,^[7] which demonstrates their high purity. Furthermore, the higher melting point of Na salts makes them easier to dry than the Li equivalents.

Thermal reactivity of Na-based electrolytes in contact with Na_x-HC

The first Na-insertion profiles of HC in various Na salts dissolved in an archetypal solvent mixture, EC/DEC, are shown in Figure 5. The HC electrodes showed similar electrochemical characteristics, with sharp slopes that start at 1.2 V, followed by well-defined small plateaus at lower potentials ($< \approx 0.1$ V) attributed to Na insertion. As reported for LIB,^[19,20] the heat released is a function of the degree of insertion (state of charge, SOC), particularly for lower values of x in Li_xC₆, which may also be expected for NIBs. Thus, all the sodiated HCs are kept at nearly the same capacity to ensure a realistic comparison of the inherent reactivity of the electrolytes.

Although neat Na salts are intrinsically stable, their fate is capricious if they exist as electrolyte solutes in contact with sodiated HC electrodes. As a figure of merit to compare the reactivity of each solvent mixture and salt, it is imperative to consider three parameters, namely, the exothermic onset temperature (related to SEI layer cracking), the temperature at which the maximum heat is released, and the total heat generated ΔH [Jg⁻¹] by the electrode/electrolyte reactions. Although the



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Table 3. Melting and decomposition temperatures of Na salts for NIB electrolytes from DSC and TGA measurements, respectively (heating rate: 10° C min⁻¹ except for NaPF₆, which was at 1° C min⁻¹). The melting points indicated in brackets refer to the corresponding Li salts.

Na salt	Anion chemical structure	τ _m [°C] (Li salt)	TGA [°C] (% mass loss)
NaPF ₆		302 (200)	400 (8.14%), 535 (74.56%)
NaClO ₄		474 (236)	500 (0.09%), 555 (2.2%)
NaTFSI		263 (234)	400 (3.21 %), 520 (85.50 %)
NaFTFSI		160 (94.5)	300 (2.75%), 420 (64.22%)
NaFSI		122 (130)	300 (16.15%), 400 (57.96%)



Figure 5. Potential–composition profiles recorded upon the first sodiation of HC in 1 μ NaX (X = PF₆, ClO₄, TFSI, FTFSI, and FSI) in EC/DEC (1:1 weight ratio).

onset exothermic temperature could be regarded as the first possible step for thermal runaway, the amount of heat released dictates the magnitude of the electrolyte decomposition in contact with Na_x-HC.

The rate of exothermic heat release of NaPF₆⁻⁻, NaClO₄⁻⁻, and NaTFSI-based electrolytes in contact with Na_x-HC decreases depending on the solvent mixture in the order of EC/PC > EC/ DEC > EC/DMC (Figure 6a–c). Hence, regardless of the nature of the salt, lower rates of exothermic heat release are recorded for the electrolytes that contain EC/PC, which shows that this mixture is suitable for safer solvent and NIB electrolyte formulations. EC/DMC and EC/DEC showed nearly the same behavior but much higher activities, which is linked to the higher reactivity of the linear carbonates (DMC, DEC) towards sodiated HC. The solubility of NaPF₆ in various single solvents has been investigated and is reported to be in the order of EC (1.4 M) > PC (1.0 M) > DEC (0.8 M) > DMC (0.6 M),^[10] which implies that NaPF₆ is coordinated more strongly by EC followed by PC in the electrolytes.

Shakourian-Fard et al.,^[21] studied the trends in the Na⁺ solvation of a variety of single solvents (EC, DMC, DEC, and EMC) and mixtures (EC/PC, EC/DMC, EC/DEC, and EC/EMC) by using classical molecular dynamics simulation and hybrid DFT calculations. A comparison of the Na⁺(EC), Na⁺(PC), Na⁺(DEC), and Na⁺(DMC) complexes evidenced the highest number of EC molecules in the first solvation sphere followed by PC and then the linear carbonates, the number of which decreases with increasing size. In EC/PC, three EC and two PC molecules were found in the primary solvation sphere. With EC/DMC, only EC molecules were found in the primary solvation sphere, whereas DMC was found in the vicinity of the highly reducing interface because of its weaker interaction with Na⁺ ions.

The improved thermal stability of EC/PC could be attributed to the intrinsic nature of the single solvents (e.g., their high polarity), in which both EC and PC are coordinated preferentially by Na⁺, which is less able to move freely and react with Na_x-HC. If NaPF₆-containing electrolytes are made with EC/DMC or EC/DEC, Na⁺ coordinates predominantly to EC to leave the more reactive DMC and DEC available to diffuse through the porous SEI layer and thereby react with the highly reducing sodiated HC at lower temperatures.

In the case of NaFSI-based electrolytes, the exothermic peak occurs at the same temperature for all solvent mixtures (Figure 6e), which shows that the thermal reactivity is mainly dictated by FSI⁻ reduction and has been reported for LiFSI-based electrolytes.^[20] Similar to LiFSI, NaFSI undergoes a two-step, four-electron reduction to produce a trication salt ($N(SO_2)_2^{3-}$) and NaF (Scheme 2). Hence, the relatively strong and energetic peak in the range of 197–207 °C is caused by the reduction of the FSI⁻, ascribed to the presence of the weak S–F bond.



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Figure 6. DSC profiles of Na_x-HC and various electrolyte formulations (which enlist the effect of the nature of the solvents): a) 1 M NaPF₆, b) NaClO₄, c) NaTFSI, d) NaFTFSI, and e) NaFSI in EC/DMC, EC/DEC, and EC/PC.

Surprisingly, the heat released by 1 M NaFSI in EC/DMC in contact with sodiated HC is only approximately half of that of 1 M LiFSI in EC/DMC in contact with lithiated graphite. This might be because 1) there might not be free Na⁺ (e⁻) to be utilized for the reduction of FSI⁻ as Na⁺ is coordinated strongly by EC and/or 2) the low degree of sodiation in HC may limit the capacity.

In the case of NaFTFSI (Figure 6d), the exothermic peaks occur at a much lower temperature than that with NaFSI independent of the solvent (or solvent mixture) used. This can be explained if we consider that the thermal behavior of the FTFSI anion (Figure 6d) resembles that of the TFSI anion (Figure 6c),

which indicates that the FTFSI and TFSI anions are not able to form a good SEI layer upon sodiation, although, according to the procedure described by Eshetu et al.,^[20] the FTFSI anion can be reduced by the anthracene radical anion (≈ 1.0 V vs. Li/Li⁺). However, the lower thermal stability of FTFSI than TFSI (Figure 4 and Table 3) results in a high heat release at lower temperatures. The response of the sample in NaFSI is rather different because this anion is able to form a robust SEI layer that protects the electrolyte salt from reduction up to much higher temperatures.

For a fixed solvent blend (e.g., EC/PC), the reactivity of Na_{x} - HC could be ranked in the order $NaFSI\!>\!NaTFSI\!>\!NaPF_6\!>$



Scheme 2. Proposed four-electron reduction of NaFSI.

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NaFTFSI > NaClO₄ with respect to the decreasing onset temperature of the exothermal process or NaFTFSI > NaPF₆ > NaClO₄ > NaTFSI > NaFSI in terms of the total heat generated (Figure 7a–c). Overall, NaFSI, NaTFSI, and NaPF₆ seem to offer the best performance if we consider the safety aspects of electrolytes for NIBs. However, NaFSI and NaTFSI are susceptible to Al corrosion and hence may not be used as single salts in electrolyte formulations.

Detailed thermal data such as the onset temperature of the first predominant exothermic peak and the total normalized heat generated for all the electrolyte formulations in contact with fully sodiated HC are summarized in Table 4.

In general, two parameters are considered if we compare the reactivity of electrolytes with Na_x-HC and the analogous Li_xC_6 : onset temperature of the exothermic reaction and total heat generation. In terms of the former, LiBs are safer than NIBs because the SEI layer of LIBs more robust. In terms of total heat generation, however, NIBs appear to be slightly better than LIBs, but the difference in the degree of lithiation and sodiation prevents us from concluding whether Na- or Libased carbonaceous electrodes are safer in terms of the power they release.

Thermal reactivity of model SEI compounds with Na salts/ electrolytes

The cascading thermal reactions of lithiated graphite are initiated by SEI decomposition at ≈ 90 °C.^[20,22,23] The origin of this decomposition is reported to be either caused by an acidbase reaction of the SEI compounds with Lewis acid species (PF₅, HF, POF₃, etc.) [Eqs. (4)–(6)] and/or the transformation of metastable SEI compounds into more stable ones [Eqs. (7) and (8)].

$$\mathsf{PF}_5 + \mathsf{Li}_2\mathsf{CO}_3 \to 2\,\mathsf{LiF} + \mathsf{POF}_3 + \mathsf{CO}_2 \tag{4}$$

$$PF_5$$
+trace $H_2O \rightarrow 2 HF + POF_3$ (5)

$$2\,HF + Li_2CO_3 \rightarrow 2\,LiF + H_2O + CO_2 \tag{6}$$

$$(CH_2OCO_2Li)_2 \to Li_2CO_3 + C_2H_4 + CO_2 + 1/2O_2$$
(7)

$$2 \text{ ROCO}_2 \text{Li} \rightarrow \text{Li}_2 \text{CO}_3 + \text{CO}_2 + \text{R} - \text{R} + 1/2 \text{ O}_2 \tag{8}$$

If we consider the high thermal stability of $NaPF_{6^{\prime}}$ however, it would be irrational to assume that the generation of PF_5 at such a low temperature and the initiation of the SEI layer



Figure 7. DSC profiles of Na_x-HC and various electrolyte formulations (which enlist the effect of the nature of the anions): 1 \times NaX (X = PF₆, ClO₄, TFSI, FTFSI, and FSI) in a) EC/DMC, b) EC/DEC, and c) EC/PC.

Table 4. Summary of the thermal parameters extracted from the DSC measurements for all the above-mentioned electrolyte formulations in the presence of fully sodiated HC.

Electrolyte system salt	solvent mixture	Onset temperature of first exothermic peak [°C]	T _{max} to first peak [°C]	Total heat generated [J g ⁻¹]
NaPF ₆	EC/DMC	75	105	257
	EC/DEC	80	123	494
	EC/PC	135	187	316
NaClO ₄	EC/DMC	60	85	733
	EC/DEC	70	90	388
	EC/PC	105	170	232
NaTFSI	EC/DMC	82	144	512
	EC/DEC	105	169	240
	EC/PC	115	201	140
NaFSI	EC/DMC	145	197	486
	EC/DEC	152	202	238
	EC/PC	159	207	50
NaFTFSI	EC/DMC	82	144	715
	EC/DEC	105	169	538
	EC/PC	115	201	414

cracking are caused by the aforementioned acid–base reactions. To verify this hypothesis and thereby to gain more insight, a DSC investigation of Na_2CO_3 mixed with $NaPF_6$, $NaClO_4$, NaTFSI, NaFTFSI, and NaFSI was performed (Figure 8a–e). The

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Figure 8. DSC profiles of powder and electrolyte mixtures (1:1 molar ratio) of a) $Na_2CO_3+NaFSI$, b) $Na_2CO_3+NaFFSI$, c) $Na_2CO_3+NaCIO_4$, d) $Na_2CO_3+NaFFSI$, e) $Na_2CO_3+NaPF_6$ and f) $Na_2CO_3+NaPF_6$ in EC/DEC.

results suggest that there is no discernible reactivity between the Na salts and Na₂CO₃ within the temperature range tested. Unlike mixtures of Li₂CO₃ with LiPF₆ and 1 M LiPF₆ in EC/DMC^[20] that show noticeable exothermic peaks around 90°C, the Na₂CO₃/NaPF₆ mixture did not show any exothermic event, which evidences that the SEI layer cracking in NIBs could not be triggered by a simple acid-base reaction and reaffirms the absence of PF₅ generation (from NaPF₆) at such a low temperature. However, one can object that the solid (e.g., Na2CO3)-gas (e.g., PF₅) reaction may not reflect the actual reactivity of PF₅ towards Na₂CO₃ realistically in NIB cells. To validate this, the DSC evaluation of Na₂CO₃ mixed with NaPF₆ in EC/DEC was performed (Figure 8 f). As a result of the strong solvation strength of EC for Na⁺, one may assume that the release of PF₅ is facilitated. However, once again, the results oppose this hypothesis. Thus, the thermal breakdown of the SEI layer in NIBs could be caused by the simple transformation of metastable SEI compounds (e.g., NEDC) into more stable ones [Eq. (9)].

$$(CH_2OCO_2Na)_2 \rightarrow Na_2CO_3 + C_2H_4 + CO_2 + 1/2O_2$$
(9)

Conclusions

A comparative investigation of diverse Na-based electrolytes that comprise various NaX $[X = PF_{6r} ClO_4, bis(trifluoromethane-sulfonyl)imide (TFSI), fluorosulfonyl-(trifluoromethanesulfonyl)imide (FTFSI), and bis(fluorosulfonyl)imide (FSI)] salts and alkyl carbonate blends [ethylene carbonate (EC)/dimethyl carbonate (DMC), EC/diethyl carbonate (DEC), and EC/propylene carbonate (PC)] and ionic liquids (Pyr₁₄FSI, Pyr₁₄FTFSI, and Pyr₁₄TFSI; Pyr₁₄=$ *N*-butyl-*N*-methylpyrrolidinium) as solvents was performed by using various analytical tools. A detailed study of the Al corrosion, formation of soluble solid–electrolyte inter-

phase (SEI) telltales, and reactivity with sodiated hard carbon (HC) enabled the screening of electrolytes for safe and performance-inspired sodium ion battery (NIB) applications.

The results can be summarized as:

1) The stability of the Al current collector in various Nabased electrolytes depends on both the salt anion and the solvents. In particular, the PF_6^- anion in organic carbonate solvents and TFSI-based IL solvents were the best electrolyte choices.

2) The generation of soluble SEI telltales depends heavily on the linear carbonates (DMC vs. DEC) and battery chemistry (Li⁺ vs. Na⁺). Unlike DMC, the reduction of DEC in NIBs was limited by the higher half-reduction potential compared to that of lithium ion batteries (LIBs).

3) The comparative reactivity study of the various Na-based electrolytes in contact with Na_x-HC shows that solvent blends that contain linear carbonates present lower onset temperatures for the exothermic process. Thus, for a fixed Na salt, the reactivity of solvent mixtures decreases in the order of EC/DMC > EC/DEC > EC/PC. The salt also plays a major role, and the reactivity decreases in the order NaClO₄ > NaFTFSI > NaPF₆ > NaTFSI > NaFSI for a fixed solvent mixture.

4) Differential scanning calorimetry analysis of Na_2CO_3 (a model SEI compound) mixed with $NaPF_6$ and $NaPF_6/EC/DEC$ revealed that the origin of the SEI layer cracking on HC differs from that of graphite.

In summary, besides the screening of safety and extrapolated performance for NIB electrolytes, our study could help to clarify the confusing remarks that exist in the literature with regard to the comparative reactivity of NIB and LIB electrolytes. Moreover, although practical validation by the assembly of large-scale NIB cells is needed, we can conclude at this stage that the SEI layer in NIBs is less robust, which leads to a lower onset temperature of the exothermic reaction and probably early thermal runaway, compared to that of LIBs.

Experimental Section

Electrolyte preparation

All tested electrolytes consist of 1 m solution of salts, namely, NaPF₆, NaClO₄, NaFSI, NaFTFSI, and NaTFSI dissolved in EC/DMC, EC/DEC, and EC/PC, all prepared in a 1:1 weight ratio. DMC, DEC, and EC from UBE Europe GmbH, Germany, and PC from BASF USA were used as received to prepare the solvent blends. The IL-based electrolytes used in this study, namely, NaFSI/Pyr₁₄FSI, NaFTFSI/Pyr₁₄FTSI, and NaTFSI/Pyr₁₄FTSI, were prepared in a 1:9 molar ratio. The ILs and salts were first dried by using a turbo pump at $\approx 10^{-8}$ mbar for ≈ 72 h. Binary mixtures of solvents were prepared carefully inside an Ar-filled drybox (O₂ and H₂O < 0.1 ppm). All salts were vacuum dried before use.

Electrochemistry

Cell assembly and cycling

For thermal analysis, Swagelok-type half-cells composed of 90 wt% HC and 10 wt% Super P carbon (no binder) as the working composite electrode (\approx 10 mg), an electrolyte-impregnated Whatman GF/



D borosilicate glass fiber as the separator, and a sodium metal foil as counter electrode were used and assembled inside an Ar-filled glovebox (O_2 and $H_2O < 0.1$ ppm). Once assembled, the cells were subjected to C/20 galvanostatic discharge/charge in the potential window of the open-circuit voltage (OCV) to 0.005 V vs. Na/Na⁺.

For GC–MS analysis, Swagelok cells were composed of a NaN₃ sacrificial salt that contained Bellcore-type 2.5 mAh film (NaN₃, Super P carbon, and polyvinylidene difluoride-hexafluoropropylene (PVDF-HFP) in a weight ratio of 69:12:19) as the positive electrode and 9 mg of 90 wt% HC and 10 wt% Super P carbon composite powder as the negative electrode. The two Whatman GF/D borosilicate glass fiber separators were impregnated with a fixed amount of 160 μ L electrolyte. The cells were subjected to a C/50 galvanostatic charge in the potential window of OCV to 3.8 V vs. Na/Na⁺.

The HC used in this work for the study of the reactivity of the electrolytes was prepared following the procedure described in Ref. [24] by the pyrolysis of biomass waste at 1100 °C for 6 h under Ar flow. The annealed powder was ground manually and ball milled for 3 h in a zirconium oxide ball mill jar (ball to powder weight ratio: 10:1) at the main disk rotation speed of 400 rpm (main rotating disc) and a reversed planetary rotation speed of 800 rpm (rotating planets). For GC–MS analysis, a low-surface-area HC (2.8 m²g⁻¹) was used to allow a fair comparison with the graphite used for LIBs.

Anodic behavior of Al

The anodic behavior of Al in all the aforementioned Na salts dissolved in EC/DEC (chosen as a representative solvent mixture) and ILs was determined by using CV. The experimental setup consisted of a three-electrode Swagelok cell in which an Al sheet rinsed with ethanol and vacuum dried served as the working electrode and metallic sodium served as both the counter and reference electrodes. Typically, the cell was left at OCV for at least 3 h before cycling at a sweep rate of 10 mV s⁻¹ between 0.1 and 5.3 V vs. Na/Na⁺.

GC-MS and FTIR spectroscopy

The HC-based electrode and the two separators were recovered after disassembling the cycled Swagelok cells inside an Ar-filled drybox. The recovered samples were treated with 1 mL of dry acetonitrile (H₂O < 0.001%), filtered, and diluted 100 times before injection into the GC–MS. GC, which was interfaced with an ISQ mass spectrometer, was performed by using a trace 1300 series GC ultra-gas chromatograph. The chromatographic separation was performed by using a "BPX70" cyanopropylpolysilene-siloxane-based capillary column (30 m × 0.25 mm i.d., 0.25 μ m) from SGE.

For the FTIR measurements, once the HC-based cells were in the desodiated state, they were opened inside an Ar-filled drybox, and the recovered powders were rinsed three times with DMC to eliminate most of the solvents and salts before they were dried in the antechamber. FTIR spectra were recorded on KBr pellets by using a Nicolet Avatar 370DTGS spectrometer.

TGA and DSC

Once the cells were in the sodiated state, they were dismantled carefully inside a drybox and the samples recovered were transferred into Al pans, and used then directly for DSC analysis. All the DSC experiments were conducted by using a Netzsch DSC 204F1

heat flux differential calorimeter at a heating rate of 10 K min⁻¹ in the temperature range of 25-500 °C under a constant Ar flow of 200 mL min⁻¹. To ensure reproducibility, two DSC measurements were conducted on each sample.

TGA tests were performed by using a Netzch instrument to $\approx 580\,^\circ\text{C}$ at $10\,^\circ\text{C}\,min^{-1}$ under a N_2 atmosphere.

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