



A non-aqueous sodium hexafluorophosphate-based electrolyte degradation study: Formation and mitigation of hydrofluoric acid

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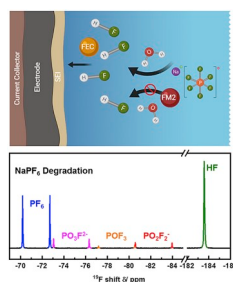
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HIGHLIGHTS

- NaPF₆-based nonaqueous electrolytes are highly susceptible to HF with water presence.
- NMR reveals an autocatalytic hydrolysis pathway of PF₆⁻ to form HF.
- FM2 can serve as an HF scavenger to improve electrolyte chemical stability.
- HF mitigation is closely related to the chemical stability of NaPF₆.
- HF formation is observed in battery grade electrolytes with <20 ppm H₂O.

GRAPHICAL ABSTRACT



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ABSTRACT

Fundamental characterization of battery electrolyte is vital for rechargeable batteries. This work reports the chemical stability of sodium hexafluorophosphate (NaPF₆)-based non-aqueous electrolytes containing different solvent mixtures (e.g., cyclic and acyclic carbonates) in the presence of water for Na-ion batteries. A degradation study is conducted using NaPF₆-based electrolytes, highlighting two electrolyte additives, 2,2,2-trifluoroethoxy-2,2,2-ethoxy phosphazene (FM2) and fluoroethylene carbonate (FEC), on degradation and cell performance of Na-ion batteries. Hydrolysis of NaPF₆ in acidic condition is particularly prone to form hydrofluoric acid (HF), and can be observed in electrolytes made with battery grade carbonate solvents (<20 ppm of water). Degradation mechanisms of NaPF₆-based electrolytes are studied using liquid nuclear magnetic resonance (NMR). Noticeable degradation takes place in high purity electrolytes with the presence of moisture to form HF and organophosphates in timeframes below the current shelf-life of the Na electrolytes. FEC is not efficient to protect the electrodes from being exposed to HF. On the other hand, FM2 is revealed as a “scavenger” of HF, which helps stabilize the shelf life of electrolytes that might contain or become exposed to water. Our study underscores the importance to understanding the degradation of electrolyte and improving stability toward better shelf life for sodium ion batteries.

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1. Introduction

Lithium-ion batteries (LIBs) are at the forefront of current energy storage technologies offering high energy, power densities, and design flexibility that outperform various technologies [1]. However, availability and cost are current challenges [1–3]. As demand continues to grow, industry faces the depletion of raw material reserves for lithium and cobalt [3]. The challenges introduce a complex interplay of availability, production, recycling, geographical/political constraints, environmental impacts, and cost [4]. These possible issues are now a debate on whether the future energy demands can be met solely by lithium-based chemistry or if other alternatives need to be utilized. One of the most appealing options is to substitute lithium with sodium in key applications to enable a sustainable outlook due to sodium's high abundance and low cost.

There are a number of challenges associated with developing a long cycle life sodium-ion battery (SIB). An aspect that has not been fully investigated for SIBs is the electrolyte degradation and the effect of the degradation byproducts on battery performance. As learned from the development of LIB, the electrolyte plays a pivotal role to enable long cycle life and performance [5–7]. The advancement in LIBs using graphitic materials was enabled once electrolytes which formed an effective solid electrolyte interphase (SEI) were recognized [7–11]. Currently, the most commonly used electrolytes for SIB research mimic those from the lithium system. The most stable and widely used non-aqueous electrolyte for LIB is a mixture of aprotic cyclic and small alkyl branched carbonates (e.g., ethylene carbonate (EC); diethyl carbonate (DEC); ethyl methyl carbonate (EMC)) and lithium hexafluorophosphate (LiPF_6) salt [12]. Sodium hexafluorophosphate (NaPF_6) is the salt used in the Na systems which historically was expected to provide analogous chemistry to the Li system [13,14]. Nevertheless, electrolytes that perform well for Li-ion batteries may not be suitable for SIBs. Differences exist between sodium and lithium electrolytes, which include thermodynamic (e.g., solvation and desolvation), kinetics (e.g., ion mobility) and interfacial properties [13, 15–17]. It is unknown if electrolytes containing NaPF_6 salt will degrade in the same manner and behave similar to the lithium analog.

The studies of lithium-based chemistry have uncovered important physicochemical properties of electrolytes that play a key role in improving battery performance [5,18]. A great example of this effort is LiPF_6 -based electrolytes that have been extensively characterized through physical properties, degradation, and contribution to the SEI formation [12,18–21]. Detailed analyses of LiPF_6 -based electrolyte degradation have revealed that trace amount of HF can be formed due to the presence of water [22–24]. It has also been noted that water can be electrochemically reduced during the initial cycling to form a uniform and dense LiF-rich SEI layer on the surface of the electrode [25]. Degradation studies of LiPF_6 -based electrolytes and their aging processes reveal that water and other protic impurities have a detrimental effect on electrolyte stability [26–33]. Additionally, the selection and optimization of binders, additives, and salts have made a dramatic effect on the electrochemical properties and performance of LIBs. The advancement of SIBs which can achieve high cycle and calendar life requires similar knowledge of stability and physicochemical properties [34,35]. In SIBs, NaPF_6 is a salt that offers promise. It has high solubility that leads to a large number of charge carriers to be present in solution [36]. In addition, the salt is relatively stable under reductive and oxidative conditions [36]. To the best of our knowledge, no research has been done to elucidate the degradation mechanisms of NaPF_6 -based electrolytes.

Herein, we report for the first time a degradation study of NaPF_6 -based electrolytes as well as the effect of two electrolyte additives: 2,2,2-trifluoroethoxy-2,2,2-ethoxy phosphazene (FM2) and fluoroethylene carbonate (FEC) on degradation and cell performance. The water content in both battery grade (BG) and standard grade (SG) solvents is evaluated, which shows higher amount of water in all SG solvents

compared to BG solvents. Degradation mechanisms of NaPF_6 -based electrolytes are studied using liquid state nuclear magnetic resonance (NMR). The effect of additive is assessed in full-cell SIBs. Noticeable degradation takes place in high purity electrolytes with the presence of water to form HF and organophosphates in time frames well below the currently needed shelf-life of the sodium electrolytes. The fluorinated additive, FEC, is unable to protect the electrodes from the detrimental exposure of HF. On the other hand, FM2 is a “scavenger” of HF, which helps stabilize the shelf life of electrolytes that might contain or become exposed to water. This study underscores the importance to understand the degradation of electrolyte to improve its stability toward better shelf life for SIBs.

2. Experimental

2.1. Water content of carbonates

Standard grade (SG) solvents of propylene carbonate (PC, Sigma Aldrich, anhydrous, 99%), ethylene carbonate (EC, Sigma Aldrich, anhydrous, 99%), dimethyl carbonate (DMC, Sigma Aldrich, anhydrous, 99%), diethyl carbonate (DEC, Sigma Aldrich, anhydrous, 99%), and ethyl methyl carbonate (EMC, Sigma Aldrich, 99%) were tested for water content. In addition, battery grade (BG) solvents of PC (BASF, anhydrous, 99.98%), EC (BASF, anhydrous, 99.98%), DMC (BASF, anhydrous, 99.99%), DEC (BASF, anhydrous, 99.99%), and EMC (BASF, 99.4%) were obtained for water content studies. Determination of the water content was completed on a V20S Compact Volumetric KF Titrator (Mettler Toledo) by coulometric Karl Fisher titration.

2.2. Electrolyte preparation

All tested electrolytes consist of either 1.2 M or 1.0 M sodium hexafluorophosphate (NaPF_6 , Alfa Aesar) salt in pure or binary solvent mixtures (1:1 vol) of PC (BASF, anhydrous, 99.98%), EC (BASF, anhydrous, 99.98%), DMC (BASF, anhydrous, 99.99%), DEC (BASF, anhydrous, 99.99%), and EMC (BASF, 99.4%). In incremental amounts, water or aqueous 48–50% HF solution were added in the electrolyte solutions to be tested for degradation. Fluorinated cyclic phosphazene trimer (FM2) was prepared in house using previously published synthetic routes [37]. Fluorinated ethylene carbonate was obtained through Sigma Aldrich. Parallel sets of samples of each mixture were maintained at two different temperatures, room temperature (RT) and 52 °C as controlled by an environmental chamber (ESPEC).

2.3. NMR sample preparation

All electrolyte solutions were prepared in an argon filled glovebox and transferred into a polytetrafluoroethylene sleeve for storage to prevent HF, presented in the evaluated samples, from etching the glass. All PTFE tubes were cleaned before use by rinsing with DI water and acetone followed by drying in an oven at 70 °C overnight. These tubes (obtained from New Era Enterprise) were sealed in the glovebox with PTFE caps. In the case of addition of water/HF mixture the tubes were sealed, removed from the glovebox, quickly unsealed, impurity added, and resealed. The sample cell (Fig. S1) contained a 5 by 155 mm glass tube with a screw cap bulb for reference solvent storage. The desired electrolyte is contained within a 4 × 143 mm PTFE tube sealed with a cap. This liner fits within the glass caustic cell. External to the PTFE sleeve, the remaining void within the NMR tube is filled with a reference solvent of deuterated chloroform containing 99.8% atom D, 1% v/v% (SiMe_4). Data processing was completed with the software TopSpin 4.0.6 (Bruker).

2.4. NMR measurements

NMR measurements were performed employing a Bruker AVANCE

III spectrometer 300 MHz NMR operating at 300.130 MHz with a broadband probe (5 mm PA BBO probe, 300 MHz, Bruker). The ^1H and ^{13}C NMR signals were referenced to TMS signal 0.0 ppm, while the ^{19}F and ^{31}P signals were referenced with respect to the signals of PF_6^- at 72.7 ppm (^{19}F) and 146.1 ppm (^{31}P). Chemical shift data and coupling are given for compounds in electrolyte mixtures containing 1 M NaPF_6 .

- Propylene carbonate (PC): ^1H NMR (300 MHz, Neat) δ 5.03 (hex, $J = 6.50$ Hz, 1H), 4.70 (d, $J = 8.07$ Hz, 1H), 4.17 (t, $J = 7.85$ Hz, 1H), 1.53 (d, $J = 6.48$ Hz, 3H). ^{13}C NMR (75 MHz, Neat): δ 156.5, 74.6, 71.3, 18.9.
- Ethylene carbonate (EC): ^1H NMR (300 MHz, Neat) δ 4.80 (s, $J = 1.82$ Hz, 4H). ^{13}C NMR (75 MHz, Neat): δ 157.4, 66.1.
- Ethyl-Methyl carbonate (EMC): ^1H NMR (300 MHz, Neat) δ 4.38 (q, $J = 7.10$ Hz, 2H), 3.98 (s, 3H), 0.82 (t, $J = 7.11$ Hz, 3H). ^{13}C NMR (75 MHz, Neat): δ 156.3, 64.7, 54.9, 14.1.
- Dimethyl carbonate (DMC): ^1H NMR (300 MHz, Neat) δ 3.98 (s, 6H). ^{13}C NMR (75 MHz, Neat): δ 157.2, 55.1.
- Diethyl carbonate (DEC): ^1H NMR (300 MHz, Neat) δ 4.37 (q, $J = 7.20$ Hz, 2H), 1.47 (t, $J = 7.20$, 3H). ^{13}C NMR (75 MHz, Neat): δ 156.0, 64.1, 14.1.
- Sodium hexafluorophosphate (NaPF_6): ^{19}F NMR (282 MHz, Neat): δ -71.7 (d, $J = 712$ Hz, 6F). ^{31}P NMR (121 MHz, Neat): 146.1282 MHz, (sep, $J = 712$ Hz, 1P)
- 2,2,2-trifluoroethoxy-2,2,2-ethoxy phosphazene (FM2). ^1H NMR (300 MHz, Neat): δ 4.25 (m, 6H), 4.05 (m, 6H) 1.33 (m, 9H).

2.5. Electrochemistry

$\text{NaNi}_{0.4}\text{Fe}_{0.2}\text{Mn}_{0.4}\text{O}_2$ (NFM) was prepared by a solid state reaction of coprecipitated precursor $\text{Ni}_{1/2}\text{Mn}_{1/2}(\text{OH})_2$, Fe_2O_3 , and Na_2CO_3 [38]. Stoichiometric amounts of chemicals were ground for 1 h and then pressed into pellets which were then heated at 800 °C for 24 h in a Vulcan 3–550 muffle oven. Commercial hard carbon (HC) (Carbotron P, Kureha Battery Materials Japan Co. Ltd.), was obtained as a gift from Pacific Northwest National Laboratory and used directly for anode electrode preparation.

A typical coin cell fabrication for the cathodes includes preparing a slurry of 80 wt% active material, 10 wt% C65 (Timcal America Inc.), and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP). This slurry was then laminated onto aluminum foil. Similarly, the anode material was prepared in a slurry of 90 wt% active material, 5 wt% C65, 5 wt% PVDF in NMP, and laminated onto copper foil. After drying at 100 °C for about 4 h, electrode disks (15 mm) were punched and allowed to further dry under vacuum at 120 °C for at least 18 h. The mass loading of active materials for NFM cathode was between 4.26 and 4.71 mg cm^{-2} and hard carbon anode was 2.49–3.21 mg cm^{-2} . Both cathode and anode were pre-cycled in a Na half-cell before assembled into full-cell coin cells (CR2032). Half-cells were assembled in an Ar-filled glovebox (Mbraun) with $\text{O}_2 < 0.5$ ppm. These electrodes were used as the working electrode and placed opposite that of Na metal disks (15 mm). A separator (Celgard 2325) was placed between the two electrodes. An electrolyte of 1 M NaPF_6 in either EC:PC or EC:DEC was freshly mixed the day before use. The NFM electrodes were cycled 5 full cycles from 4 to 2 V, after being charged to 4 V. The HC electrodes were cycled 5 full cycles from 2 to 0.01 V. Subsequently, full cells were assembled using the pre-cycled HC anode and NFM cathode, with a capacity-based negative:positive (N:P) ratio of at least 1.1:1. Various aged electrolytes with or without additive and water were utilized in full cell testing.

3. Results and discussion

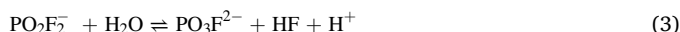
3.1. Water content in carbonate solvents (standard grade vs. battery grade)

All BG solvents exhibit water content below 20 ppm (Table 1), with many containing less than 10 ppm (the lower detection limit of the KF titration method). The water level dramatically increases for SG solvents from lowest concentration being contained with DMC of 24.6 ppm to EMC of up to 530.8 ppm. In the case of SG carbonate solvents from general chemical suppliers, it is shown that the water content is in general higher compared to BG solvents. Battery grade solvents are needed to promote high performance by limiting electrolyte degradation. The use of SG solvents increases the amount of water available to participate in electrolyte degradation. This is especially important to SIB research as commercially available Na electrolytes are scarce and the few that are available are cost prohibitive presenting barriers to many laboratories. Thus, most research labs blend their own electrolytes. The grade of solvents used is particularly important to limiting the water content in the electrolytes. For the sake of controlling the water content in the electrolytes, we used BG solvents for all electrolytes tested for the remaining degradation studies.

3.2. Degradation of electrolytes in the presence of water

Electrolytes containing PF_6^- salt are known to degrade in the presence of water through a process of hydrolysis to form HF and fluorophosphates [19,39,40]. In this work, the degradation products in BG electrolytes are monitored by NMR. After aging at 52 °C for 31 days (Fig. 1), a distinct increase in HF and phosphorus-containing salt byproducts is observed for the sample with 0.2% v/v water content.

HF is generated through hydrolysis of the hexafluorophosphate as indicated by the singlet at -183.9 ppm in Fig. 1a and c. The presence of HF is a key concern since the rate for degradation in acidic environment is significantly enhanced [41]. The increased concentration of H^+ , as noted by the increased concentration of HF can in turn facilitate an autocatalytic process which accelerates the rate of degradation. This catalytic process supported by the data in Fig. 1, is proposed through the following pathways which mirror observations in Li salts [19,23]:



For the aged BG electrolyte, only trace amounts of HF and two fluorophosphate ions, monofluorophosphate (PO_3F^{2-}) and difluorophosphate (PO_2F_2), are present (Fig. 1a and b). These two fluorophosphate ions have been noted as major products in the hydrolysis of PF_6^- , and are observed as two doublets in the ^{19}F NMR [19]. The corresponding ^{31}P spectrum exhibits a splitting pattern of a doublet (PO_3F^{2-}) and a triplet (PO_2F_2), corroborating with the results from ^{19}F NMR. To confirm the location and coupling constants of PO_2F_2 , the corresponding difluorophosphoric acid was obtained and measured in a carbonate solvent. The chemical shift and splitting pattern matched with a deviation of 0.06 ppm and 17.4 Hz. The 0.2% water containing aged electrolyte shows a dramatic increase in HF as well as four byproducts

Table 1
Comparison of water content in SG and BG carbonate solvents.

Solvent	SG H2O (ppm)	BG H2O (ppm)
Ethylene Carbonate (EC)	–	–
Propylene Carbonate (PC)	61.8	<10
Diethyl Carbonate (DEC)	47.2	11.2
Ethylmethyl Carbonate (EMC)	530.8	<10
Dimethyl Carbonate (DMC)	24.6	<10

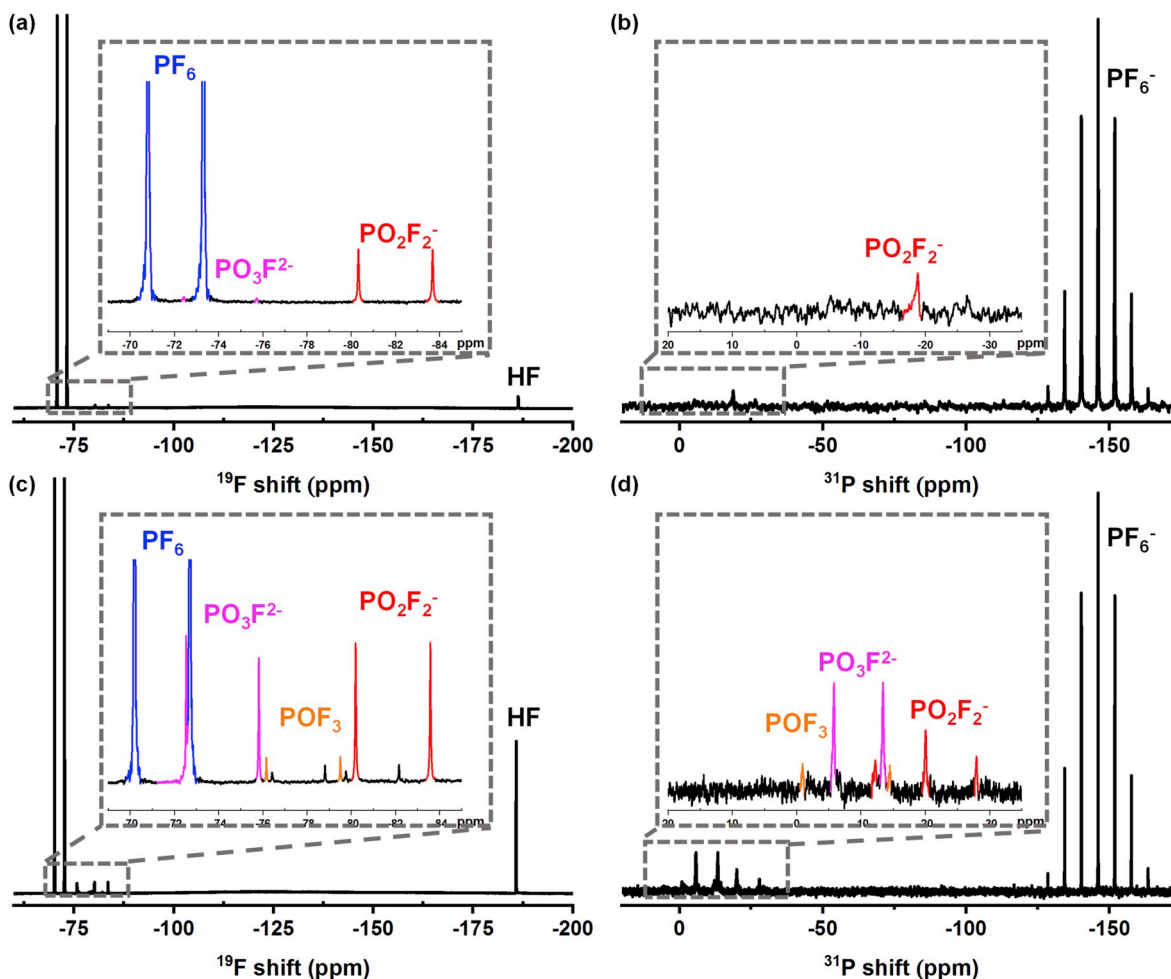


Fig. 1. ^{19}F and ^{31}P NMR spectra of thermally aged 1.2 M NaPF_6 in 3:7 EC:EMC (w/w) electrolyte for 31 days at 52 °C, BG electrolyte (a–b) and electrolyte with 0.2% (v/v) H_2O (c–d). Insets: Zoomed in spectra.

due to NaPF_6 degradation (Fig. 1c and d). These include a large amount of both PO_2F_2^- and PO_3F_2^- . The additional byproducts are possibly related to solubilized PF_5 or POF_3 gas which was observed to form in the NMR tubes (Supporting Information, Fig. S1). The fourth degradation product is the insoluble precipitate, NaF as determined by energy-dispersive X-ray spectroscopy (Supporting Information, Fig. S2). As NaF precipitates it promotes further hydrolysis. Electrolytes at room temperature with the same concentration of water took several months to show observable hydrolysis products (Supporting Information, Fig. S3). The concentration of the phosphates and HF are considerably lower (40–100 times smaller) than electrolytes held at higher temperature. This is in stark contrast to the lithium battery system where PF_6^- has been shown to degrade much faster even at room temperature [19]. To accelerate degradation, temperatures were held at 52 °C for the remaining NMR-based hexafluorophosphate degradation studies.

As expected, as the water content increases so does the concentrations of the HF and the fluorinated phosphates (Fig. 2). Increasing the water content from 0.2% to 1.25% (v/v), led to a shift in the major component of the electrolyte from PF_6^- to a mixture of degraded fluorophosphates and HF. While this level of water content is not observed in commercial electrolytes, it does suggest that the extent of degradation in an electrolyte is determined by the initial amount of water. While the abundance of the PF_6^- is held constant as shown in Fig. 2, the concentration of HF increases by 500%. In addition, the formation of PO_2F_2^- and PO_3F_2^- shows a two-fold and three-fold increase, respectively.

To better understand more realistic battery electrolyte conditions, smaller additions of water (10–100 ppm) are studied (Fig. 3). HF is

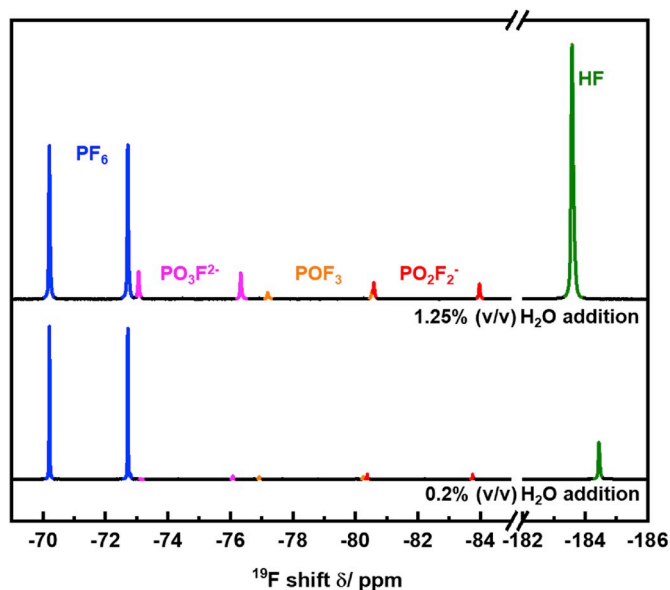


Fig. 2. ^{19}F NMR spectra of aged 1 M NaPF_6 in 1:1 EC:PC (v/v) electrolyte containing 0.2% (v/v) of water and 1.25% water (v/v) with degradation products of HF, PO_2F_2^- , POF_3 (likely), and PO_3F_2^- .

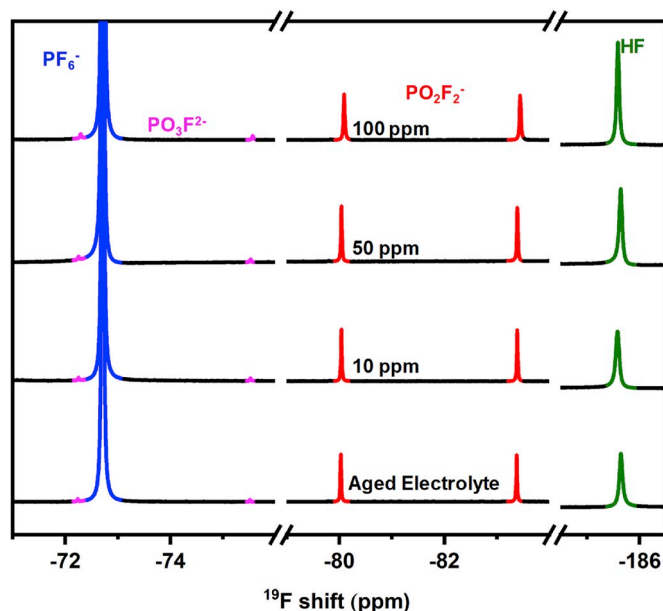


Fig. 3. ^{19}F NMR spectra of increasing water concentration from aged (31 days at 52°C) BG to 100 ppm of added water electrolytes containing 1 M NaPF_6 1:1 EC:PC.

present in every sample. After aging the electrolyte with 100 ppm added water, the HF concentration nearly doubles of that found in the pristine BG electrolyte. The concentration of fluorophosphates, PO_2F_2^- and PO_3F_2^- , only increases by a fourth compared to the pristine electrolyte. It is interesting to note the formation of these degradation byproducts in the pristine electrolyte. The pristine electrolyte of 1 M NaPF_6 in EC:PC shows water content well below the commercial standard (<20 ppm). Such result reinforces the effect that trace water can have on the degradation of NaPF_6 -based electrolytes given enough thermal energy or time.

3.3. Carbonate solvents degradation in the presence of HF

Carbonate solvent stability study is performed via ^1H NMR on five electrolyte mixtures in the presence of HF (Fig. 4). Aging the electrolytes includes the addition of a 1:1 (v/v) HF: H_2O (final concentrations of 0.125% (v/v) HF and 0.125% (v/v) H_2O). The ^1H NMR spectra were obtained after 4 weeks (or 28 days). From these results, cyclic EC is the most vulnerable form of the five tested carbonates. As demonstrated by the appearance of 1,2-ethanediol (4.05 ppm) in solvent mixtures containing EC. The most plausible formation for this alcohol is through acid catalyzed hydrolysis, which leads to decarboxylation of the cyclic EC [42–44]. The formation of 1,2-ethanediol is the only observable degradation product over the 28 day period at room temperature in the blended solvent of EC:DEC. Decarboxylation of DEC would have led to the formation of methanol and ethanol, which were not detected. The hydrolysis of DEC and EMC have been described as a completely intramolecular process, due to the degradation products of C_2H_4 and CO_2 in an equimolar ratio, and ethanol or methanol, respectively [45]. No ethanol was observed in either DEC or EMC when EC is present. Methanol formation is observed in DMC. The thermodynamically favorable degradation pathway of these alkyl carbonates is to form the corresponding alcohol with the intermediates favoring the formation of methanol before ethanol. It is plausible that the ethyl substituent does not possess the energetics to support the formation of ethanol. Similar behavior was observed for EMC containing electrolyte in which methanol is the only observable degradation product. EMC contains both ethyl and methyl moieties, though the more favorable intermediate would promote the hydrolysis reaction at the shorter alkyl branch. When

the electrolyte contains EC:PC, 1,2-ethanediol becomes the major degradation product. In addition, the electrolyte contains a small amount of 1,2-propanediol, the corresponding alcohol of PC. Based on these observations, it suggests that both the steric hindrance and the ability to act as an electron donating group of the $-\text{CH}_3$ moiety makes PC less susceptible to chemical breakdown. Based on the near equimolar ratios of solvent molecules it is clear from the results that EC is the most susceptible to proton attack. A possible explanation for this heightened susceptibility is the intramolecular stress of the five-membered ring of the cyclic carbonates, such as EC and PC. However, the steric hindrance assumed from the methyl moiety of PC improves its stability. The linear carbonates also exhibit a decreasing rate of degradation as the aliphatic chain lengths increased, $\text{DMC} > \text{EMC} > \text{DEC}$.

3.4. Full cell degradation performance

The degradation seen in the NMR data for the carbonate electrolytes poses the question of how degradation impacts overall cell cycling performance. To better understand the role of electrolyte degradation cycling performance of $\text{NaNi}_{0.4}\text{Fe}_{0.2}\text{Mn}_{0.4}\text{O}_2$ (NFM)/hard carbon (HC) full cells in the presence of degraded electrolytes with and without additives that contain 0 ppm and 100 ppm added water is shown in Fig. 5. In addition to standard and water-containing electrolyte, the role of two different additives (FM2 and FEC) is investigated. The first additive is a promising phosphazene derivative, which has proven beneficial to battery electrolytes by increasing the thermal and electrochemical stability [37]. This work also investigates FEC, a popular additive that is linked to the production of a more resilient SEI layer [46,47]. Improved resilience may lead to less impact from impurities such as HF [48]. These two additives act through one of the two methods: either mitigation of electrolyte degradation or through the production of a more resilient SEI.

Aged pristine electrolyte (black) is identical in performance of aged 5% FM2 containing electrolyte (red) (Fig. 5). In comparison, the full cell with electrolyte that contain 5% FEC (blue) exhibits a ~ 20 mAh/g capacity drop. When 100 ppm water is added with no electrolyte additives the cell (purple) retains only 14 ± 2 mAh/g after 100 cycles. This is expected as the NMR results indicate large quantities of both HF and salt degradation products with water addition. When FM2 is added (green) the initial capacity is improved to nearly 44 ± 3 mAh/g. This result indicates that mitigating the degradation of the salt in the electrolyte can prevent the battery from complete failure. For the FEC added electrolyte with 100 ppm water (cyan), the capacity is similar to the additive-free electrolyte. Insignificant HF mitigation has taken place leading to poor cycling performance. FEC has been established as a promising additive to improve hard carbon electrode performance via the formation of a more resilient SEI layer [20,47,49,50]. However, HF has been proposed as a detrimental component in electrolytes related to the dissolution of transition metals in cathode materials [51]. The dissolved transition metals can then deposit on the surface of the anode, which leads to poor cycle life performance [52–54]. From our results, it is suggested that in order to extend the shelf life of Na ion batteries it might be necessary to mitigate both the chemical stability of the electrolyte and stability of SEI using different functional additives.

3.5. Effect of additive in degradation

As indicated in the cycling data the use of FEC and FM2 present two distinctly different performance levels in full cells. To discern the role that both play in electrolyte degradation FM2 and FEC are evaluated during the degradation process (Fig. 6).

The ^1H and ^{19}F NMR results of 1 M NaPF_6 in EC:PC (1:1) with 100 ppm added water (Fig. 6a and b) indicate that FM2 acts as a “scavenger” and inhibits the formation of HF. This phosphazene additive has been used in other studies to stabilize LiPF_6 -based electrolytes at high temperatures [37]. In the absence of HF the degradation of PF_6^-

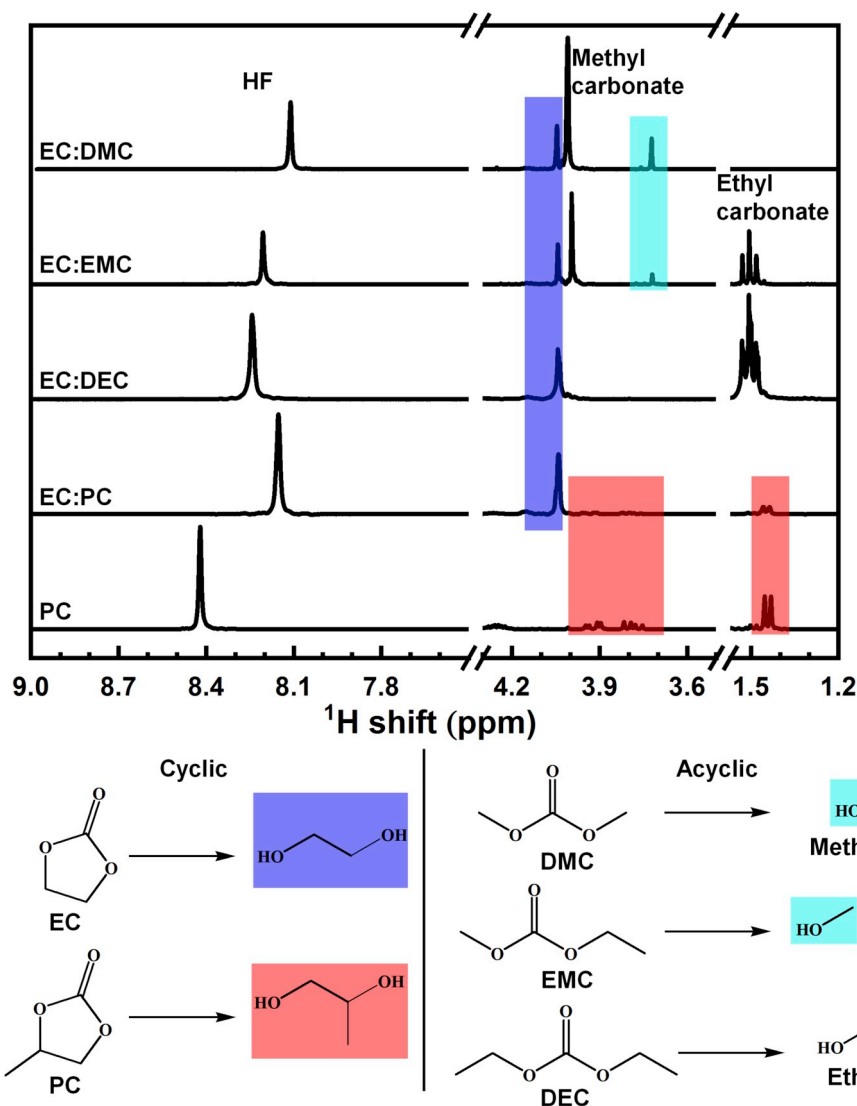


Fig. 4. Stability of carbonates in NaPF₆ electrolytes via ¹H NMR. Highlighted area: EC degradation product 1,2-ethanediol (blue), PC degradation product 1,2-propanediol (red) and EMC/DMC degradation product methanol (cyan). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

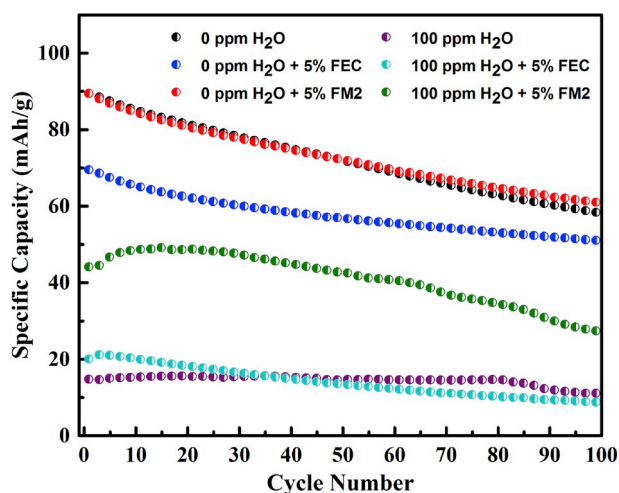


Fig. 5. Cycle life performance of 1:1 EC-PC aged electrolytes with and without additives and water.

salts is dramatically reduced. The ³¹P NMR result (Fig. 6c) suggests FM2 degradation accompanies the F⁻ formation. This in turn removes or scavenges F⁻ from the catalytic pathway of PF₆⁻ salt hydrolysis. Intrinsically, FM2 has mitigated the complete formation of HF. We believe that this result stems from the structure of the phosphazene additive, which has a cyclic ring with resonating π bonds between P and N. This structure leaves P susceptible to nucleophilic attacks from free ions in solution such as F⁻ or from H₂O. For comparison, the more commonly used FEC additive exhibits only a small effect in mitigating the degradation products. Through ¹⁹F and ³¹P NMR characterization, even with up to 10% FEC, HF concentration remains high (Supporting Information, Fig. S4).

Combining the NMR and cycle life data using elevated water content suggest that degradation of the electrolyte may be a key contributor to shortened cycle life for SIBs. While it is not anticipated that future SIBs will contain the high levels of water used here, the degradation at elevated temperatures, even for high purity solvents, suggests that formation of HF is bound to pose long-term problems for full cell performance. Thus, continuing to evolve SIB electrolyte formulations to more closely mirror what has been done in LIB systems is a logical path for future development. Specifically targeting additives such as FEC to

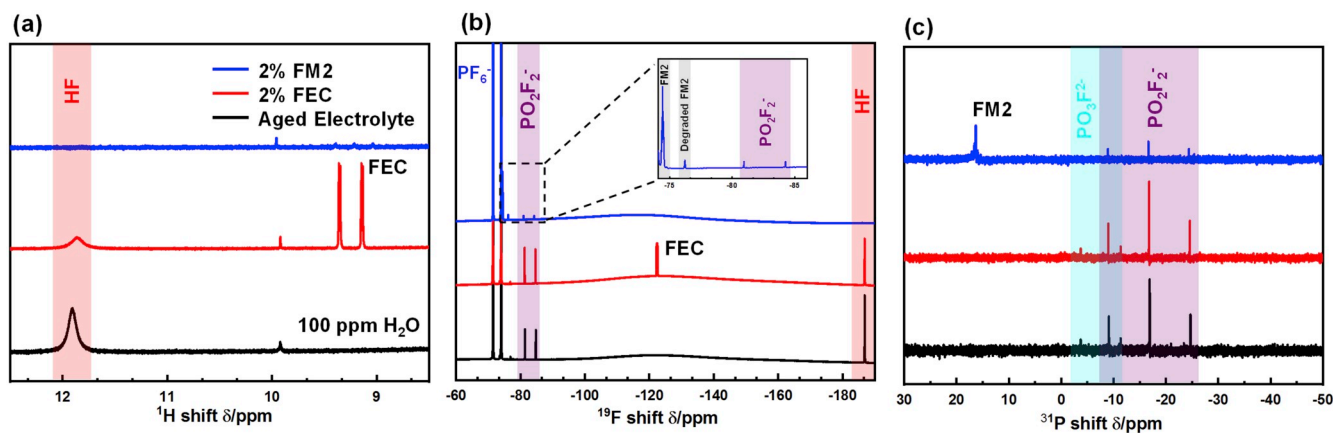


Fig. 6. (a) ^1H (b) ^{19}F (c) ^{31}P NMR spectra of 1 M NaPF_6 in EC:PC 1:1 with 100 ppm added water aged over a 31 day period at 52 °C, with no additive (black), 2% v/v FEC additive (red), 2% v/v FM2 (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

increase SEI stability and FM2 to mitigate salt breakdown are likely to continue to advance SIBs into the cycle life realm that is needed to be effective in many applications of interest including stationary energy storage.

4. Conclusion

Water has a dynamic, significant role in the stability of NaPF_6 -based non-aqueous electrolytes for sodium ion batteries. These electrolytes are highly susceptible to the formation of HF in the presence of water. Most remarkably, HF formation can be observed in BG electrolytes which contain <20 ppm H_2O . The NMR results demonstrate an autocatalytic hydrolysis pathway of hexafluorophosphate to form HF in the electrolyte. Byproducts of the salt degradation, PO_3F_2^- and PO_2F_2^- , are also confirmed with NMR. It is acknowledged that these species may play a dramatic role in the stability of the electrolyte. The most vulnerable carbonate solvent is shown to be cyclic EC. In comparison, PC clearly shows a slower rate of degradation. The rate of decarboxylation of the acyclic carbonate species depends on the length of the aliphatic chain (i. e., $\text{DMC} > \text{EMC} > \text{DEC}$). Electrolytes with and without added water are tested in full-cell batteries of NFM cathode and hard carbon anode with FM2 and FEC. The full cell with aged electrolyte with no added water and containing FM2 shows comparable performance to aged pristine electrolyte without added water at 91 ± 0.5 mAh/g. In comparison the full cell with FEC demonstrates a dramatic decrease in initial capacity. When water is added (100 ppm), the capacity drastically decreases to 14 ± 2 mAh/g, similar to the additive-free electrolyte. Remarkably, when FM2 is present in the aged electrolyte with added water the full cell has an initial capacity of $\sim 44 \pm 3$ mAh/g and an overall capacity retention of 62% at 100 cycles. This verifies that the byproducts of the salt degradation are detrimental to the performance of a sodium ion battery. This study links HF mitigation and the chemical stability of the NaPF_6 -based non-aqueous electrolytes. In the research and development of sodium ion battery technologies, electrolytes should be closely monitored for degradation. Similarly, additives such as FM2 should be considered to increase the stability of the electrolyte. Stabilizing the electrolyte and mitigating the degradation of the electrolyte could promote the shelf life and performance sodium ion batteries.

Author contributions

HX, PB, and ED conceived and designed all experiments. KS and RP conducted the physiochemical properties characterization. PB, DK, CJ, CD, ES, PS, ML and QW fabricated electrodes for the full cell. PB, JD, and DK conducted all electrolyte degradation monitoring via NMR. ML prepared solid work digital diagrams. PB conducted all electrochemical

measurements. PB conducted electron dispersion spectroscopy. PB, HX, and ED wrote the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jpowsour.2019.227363>.

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