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# **Non-aqueous electrolytes for Na-ion batteries: Challenges and prospects towards commercialization.**

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## **Abstract:**

Integration of Na-ion batteries (NIBs) as a complementary energy storage device to the presently dominating Li-ion battery technology is a must, considering the cost and sustainability issues of lithium. However, despite the important laboratory-scale achievements concerning Na-ion electrodes and electrolytes, the improvements needed for realizing battery devices to meet users demands are being relatively slow. More specifically, the development of suitable electrolytes remains as the bottleneck that restrains this technology from meeting the commercial requirements, hence defining a future challenge. This review explains the design strategies in use for NIB electrolytes with a special emphasis on intrinsic differences between Li- and Na-ion chemistries, which are at the origin of difficulties associated with the discovery of optimum electrolytes for NIBs. We highlight the key requirements that an electrolyte must satisfy and related experimental techniques that could be used for quick screening of NIB electrolytes in laboratory-scale for exploiting in commercial NIB devices.

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## 1. Introduction: Towards the transition from Li- to Na-ion batteries

Li-ion battery (LIB), as energy storage device, is one of the indispensable daily utilities at present. Owing to more than 25 years of intensive research in LIB materials and engineering, in addition to the discovery of new Li-resources, the technology has witnessed an important cost drop in the recent years. Yet, considering the growing demand on LIBs in the market, which is foreseen to increase in the coming years, the need for coming up with cheaper and more sustainable energy storage devices is essential. To this end, NIBs represent an attractive alternative as they not only share analogous chemistry with LIBs, but also same engineering and production equipment as well.<sup>[1]</sup> Indeed, the progress in NIBs is going relatively faster compared to the other beyond LIB technologies (*e.g.* Li-air/ S, K/ Ca/ Mg-ion batteries, etc), and prototypes of Na-ion cells have already been demonstrated in both 18650 (TIAMAT, France) and pouch type (Faradion, UK and Novasis, US etc) cell formats.<sup>[2][3]</sup> The Na-ion cells demonstrated so far uses predominantly hard carbon as negative electrode and inorganic material such as polyanionic  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ , sodium layered oxide or Prussian blue (white) analogs as positive electrode.<sup>[3][4][5]</sup> Organic materials as positive electrode (*e.g.* quinones)<sup>[6][7]</sup> though under vigorous research is avoided for now in real-life NIB applications, due to their intrinsic disadvantages such as low conductivity, low redox potential and solubility of the electrode material in electrolytes.

A specific energy of  $\sim 140 \text{ Wh kg}^{-1}$  is reached using inorganic positive electrode and hard carbon negative electrode, which is close to that of  $\text{LiFePO}_4$ //graphite-based Li-ion cells ( $\sim 160 \text{ Wh kg}^{-1}$ ).<sup>[2]</sup> The larger mass and the slightly lower reduction potential of  $\text{Na}^+$  compared to  $\text{Li}^+$  ( $-2.71$  vs  $-3.05 \text{ V vs NHE}$ ), ultimately imply lower energy densities in NIBs than in their LIBs analogues.<sup>[1]</sup> Nevertheless, the achieved specific energy of  $\sim 140 \text{ Wh kg}^{-1}$  in NIBs combined with the advantage of sustainability is an inducement for further advancing the technology and realizing its commercialization, provided that it could satisfy other end-users demands.

The major end-user demands could be summarized as (a) thermal stability and safety, (b) operation in all climatic conditions, (c) fast charging capability and (d) minimal self-discharging when at rest.<sup>[8]</sup> More importantly, considering the safety concerns that even the well-mature LIB technology suffers from, with reported fire accidents,<sup>[9]</sup> it is of paramount importance to early address this issue in the emerging NIB technology before moving towards commercialization.

Interestingly, all the aforementioned aspects though partly depend on the nature of electrode material in use, they are mainly controlled by the involved electrolyte hence making the electrolyte optimization as the key step towards commercialization of NIBs. So, in this review, we summarize the electrolyte design principles that must be followed during selection of electrolytes for NIBs dedicated for real-life applications, in addition to the suitable laboratory scale techniques that could be utilized for quick screening. We underlie the practical difficulties that hamper the design of the suitable electrolyte for NIBs while hoping to contribute to the efforts aiming to identify possible strategies to overcome them.

## **2. Electrolytes for Na-ion batteries**

### **2.1. Basic principles and designs**

Electrolyte is a major component of the Na-ion battery that ensures  $\text{Na}^+$ -ion diffusion from positive to negative electrode and vice versa while restricting the conduction of electrons through it. In order to enable an efficient operation of a battery, several necessary characteristics must be available in the electrolyte such as low viscosity, high conductivity and electrochemical stability. All these properties have been widely explored by the LIB research community. For instance, mixture of cyclic and linear carbonate based solvents (esters) were found to exhibit the optimum behavior together with a Li- inorganic salt (eg.  $\text{LiPF}_6$ ,  $\text{LiClO}_4$  etc) as a supporting electrolyte and are termed hereafter as ‘conventional electrolytes’ as they are routinely used in commercial LIBs. In this electrolyte formulation, cyclic carbonates such as ethylene carbonate (EC) possess high dielectric constants thus helps in dissociating  $\text{Li}^+$  ion from the anion (eg.  $\text{PF}_6^-$  in  $\text{LiPF}_6$ ).<sup>[10]</sup> This property is an advantage for the battery operation since it assists the conduction of the alkali ( $\text{Li}^+$ / $\text{Na}^+$ ) cation through solvation. On the other hand, linear carbonates such as Dimethyl carbonate (DMC), often used as co-solvents, help in reducing the viscosity of the electrolyte.

Similar design principles were quickly adopted for NIB electrolytes as well and studies were conducted on different sodium salts with varying concentrations in non-aqueous organic solvent(s).<sup>[11]</sup> The inorganic sodium salts namely sodium hexafluorophosphate ( $\text{NaPF}_6$ ),<sup>[12][13]</sup> sodium perchlorate ( $\text{NaClO}_4$ ),<sup>[14]</sup> imides such as sodium bis(trifluoromethanesulfonyl)imide ( $\text{NaN}(\text{CF}_3\text{SO}_2)_2$  termed NaTFSI) and sodium bis(fluorosulfonyl)imide ( $\text{NaN}(\text{SO}_2\text{F})_2$  termed NaFSI),<sup>[15]</sup> sodium trifluoromethanesulfonate ( $\text{NaCF}_3\text{SO}_3$  termed NaOTf),<sup>[16]</sup> sodium

tetrafluoroborate ( $\text{NaBF}_4$ ),<sup>[17]</sup> sodium bis(oxalate)borate ( $\text{NaBOB}$ )<sup>[18]</sup> and sodium difluorooxalato borate ( $\text{NaODFB}$ )<sup>[19]</sup> etc were investigated as supporting electrolyte in different organic solvent(s) as well as in ionic liquids<sup>[17]</sup>. Nevertheless, the ionic liquid as solvent is usually expensive and in use mainly for special applications where safety is the main concern and not the cost. Hence, ionic liquid based electrolytes are categorized under ‘non-conventional electrolytes’ and are discussed at the end of this review article.

Among the studied conventional organic solvents, organic carbonate based electrolytes exhibit good solubility for  $\text{NaPF}_6$ ,  $\text{NaClO}_4$  and  $\text{NaBF}_4$  etc and ionic conductivity of 6- 10  $\text{mS cm}^{-1}$  is achieved for 1M solution at 25 °C.<sup>[11]</sup> Since the usage of  $\text{NaClO}_4$  is avoided due to its possibly explosive nature,<sup>[11]</sup>  $\text{NaPF}_6$  in a mixture of cyclic- linear carbonate solvents is the most preferred electrolyte formulation for NIBs in research<sup>[12]</sup> as well as in the start-up companies.<sup>[3]</sup> Moreover, the simulation studies on lithium/ sodium/ potassium solvation in ethylene carbonate shows weaker solvation for  $\text{Na}^+$  and  $\text{K}^+$  ions than  $\text{Li}^+$  with solvation energies being 5.85, 4.72 and 4.12 eV for  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  respectively.<sup>[20]</sup> Such results predict the faster  $\text{Na}^+$ -diffusion hence better ionic conductivity for  $\text{Na}^+$  in ethylene carbonate than  $\text{Li}^+$ , which is an added advantage for NIBs for high power application. Recently, more studies are devoted to low viscosity solvents such as ethers with the aim to reach highest ionic conductivity.<sup>[21]</sup> However, the ethers are limited by their poor electrochemical stability window, in which esters stand out to be the best due to the formation of stable interphase.

## **2.2. Electrochemical stability of electrolytes through the formation of stable interphases**

In order to reach high energy batteries, it is important to use electrodes of high redox potential. In such case, the electrolyte is often less stable within the used voltage window and the electrolyte solvent molecules electrochemically decompose at the positive and negative electrodes. If this process is not controlled at a given time, the continuous decomposition of the solvent will eventually lead to cell failure.<sup>[22]</sup> Fortunately, in the ideal case, this decomposition process stops due to the growth of the electronically insulating thin protecting layers known as solid-electrolyte interphase (SEI) and cathode-electrolyte interphase (CEI) at the interface between the electrolyte and the negative/positive electrodes respectively.<sup>[23]</sup> Such interphases kinetically extend the electrochemical stability window of the solvent. The chemical composition of these interphases is derived from the electrolyte (i.e. solvent+ salt) solid decomposition products that deposit on the electrode surfaces leading to their passivation. In fact, the SEI and CEI must satisfy few

conditions to ensure the desired operation of the battery. While electronically insulating, the interphases must be ionically conductive in order to secure a facile infiltration of the shuttling cation to and from the electrodes during charging/discharging cycles. In addition, they have to be insoluble, chemically inert and mechanically robust. If the SEI/ CEI fail to fulfill these demands, the battery in question will experience an inevitable deterioration in the performance. In LIBs, the carbonate-based electrolytes demonstrated huge success, where the cyclic ethylene carbonate reduces on the negative electrode (graphite) to form a stable and ionically conducting SEI that accounts for the long cycle life of LIBs hence their huge success in the market. So, the question is, can we expect the same for carbonate-based electrolytes in NIBs?

### **3. Transferring knowledge from LIBs- to NIBs electrolytes**

The ability of carbonate-based solvents in assisting the formation of SEI/ CEI with required properties in LIBs spontaneously cast a shadow on the selection process of electrolyte components in the new battery technologies especially NIBs. Thus, the electrolyte constituting of 1M NaPF<sub>6</sub> in EC:DMC (1:1 v/v), denoted hereafter by NP30, was employed as the sodium version of LP30 (i.e. 1M LiPF<sub>6</sub> in EC-DMC (1:1 v/v)). Using NP30 as electrolyte in Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3</sub> (NVPF)/ Hard carbon (HC) cell assembled in 18650 format, Broux et al. reported a long cycle-life at room temperature with capacity retention of ~80% after more than 4000 cycles.<sup>[24]</sup> On the other hand, Guochun et al. reported poor cycle life and self-discharge performances at high temperatures.<sup>[24]</sup> Nevertheless, considering the local temperature changes within the cell during its operation, it is essential to maintain stable cycling at high temperatures. The authors concluded that the decomposition products of linear carbonates on the hard carbon electrode dissolve and shuttle towards the NVPF positive electrode resulting in the degradation of the cell performance. Whereas, linear carbonates are extensively used in LIBs without any such phenomenon reported. This inferior behavior of NP30 in NIB with respect to that of LP30 in LIB points towards the poor stability of interphases in NIBs.

#### **3.1. Intrinsic differences between Li<sup>+</sup> and Na<sup>+</sup> and the consequences on the respective electrolyte behaviors**

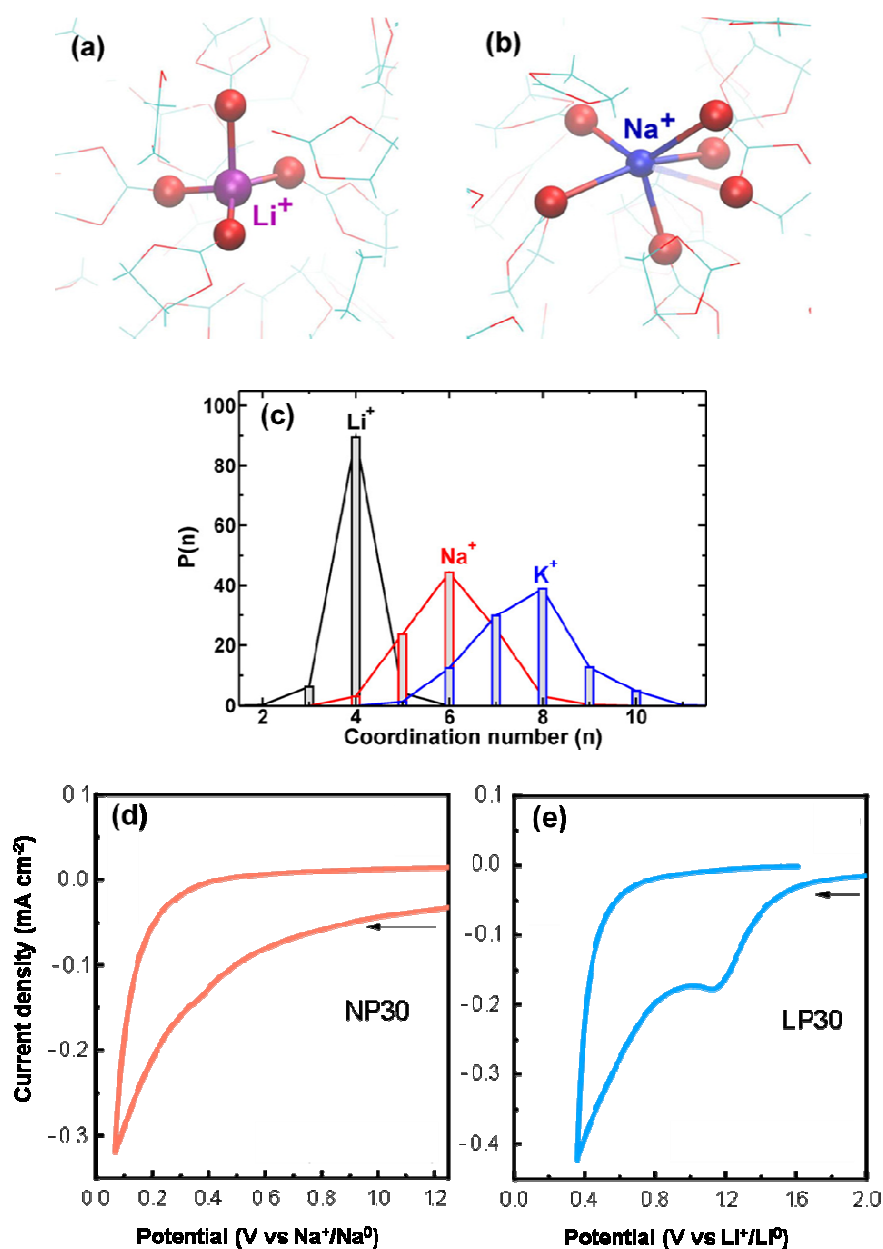
It is widely accepted that the SEI generated from sodium-based electrolytes is much vulnerable than that generated from lithium-based analogues.<sup>[25]</sup> One possible reason could be the difference

in solubility of the Li and Na-products that compose the SEI. Even by starting from the same solvent system (e.g. EC-DMC) and the same salt counter-anion (e.g.  $\text{PF}_6^-$ ), the  $\text{NaPF}_6$  based electrolyte result in a considerably soluble SEI compared to the one formed from the  $\text{LiPF}_6$  analogue. This behavior originates from the modification in the physicochemical properties when moving from  $\text{Na}^+$  to  $\text{Li}^+$ . In fact, apart from both being monovalent positively charged, the cationic radius of  $\text{Na}^+$  (102 pm) is larger than that of  $\text{Li}^+$  (76 pm). Consequently, the charge density (charge/radius ratio) on the  $\text{Na}^+$  is considerably lower than on  $\text{Li}^+$  which makes it a weaker Lewis acid. The larger cationic radius and weaker Lewis acidity yield a different coordination/bonding behavior of  $\text{Na}^+$  with other atoms or molecules. The  $\text{Li}^+$  is known to be involved in highly stable organometallic compounds due to the covalent character of the bonds it forms with ligands. There are some literature data that report *ca.* 20% weaker binding energies of  $\text{Na}^+$  complexes compared to the  $\text{Li}^+$  analogues because of its lower charge/radius ratio.<sup>[26]</sup> Accordingly, there are several indications that allow us to perceive sodium salts contributing to the SEI composition as considerably more soluble than their counterparts in the SEI derived from a  $\text{Li}^+$ -based electrolyte. For instance,  $\text{Na}_2\text{CO}_3$  and  $\text{NaF}$ , which are often detected as major components of the Na-derived SEI, are reported to be more soluble than the  $\text{Li}_2\text{CO}_3$  and  $\text{LiF}$  counter-parts in a Li-derived SEI.<sup>[27]</sup> Moreover, the aforementioned differences between  $\text{Na}^+$  and  $\text{Li}^+$  also have consequences on their solvation/de-solvation behaviors that govern their respective SEI chemistries. The  $\text{Li}^+$  is predicted to have a coordination number (CN) of 4 versus CN=6 for  $\text{Na}^+$  (Figure 1(a-c)) in electrolytes at conventional concentrations (i.e.  $\sim 1\text{M}$ ).<sup>[20]</sup> In carbonate-based solvents, cyclic carbonates (e.g. EC or PC) dominate the process of solvation of cations in the primary solvation sheath due to their higher dipole moment where the lone-pair electrons of the carbonyl oxygen stabilize the Coulombic attraction of the small cation. Thus, if an EC-DMC solvent is adopted, the coordinating EC molecules in LP30 will be more electron deficient than the coordinating EC molecules in NP30. Thus, the participation of EC molecules in the SEI chemistry in LP30 is more favored than in NP30 due to the facilitated electrochemical reductive decomposition. Accordingly, important difference in the properties of SEI derived from the homologous electrolytes is expected.

### 3.2. Isolating the impact of the electrode material on the SEI properties



Moreover, the different electrode active materials, graphite and hard carbon negative electrode used in LIBs and SIBs respectively, makes difficult the direct detection of such disparities between  $\text{Li}^+$ - and  $\text{Na}^+$ -based electrolytes in cell mode since the process of SEI formation is also a function of the involved active material. In an attempt to eliminate the impact of the electrode material and investigate the effect of the involved cation on the electrochemical behavior of the electrolyte, we adopted cyclic voltammetry (CV) experiments.<sup>[28]</sup>



**Figure 1.** Scheme representing the solvation structures of (a)  $\text{Li}^+$ , and (b)  $\text{Na}^+$  derived from molecular dynamic simulations showing tetrahedral (CN= 4) and trigonal bipyramidal/ square pyramidal (CN= 6)

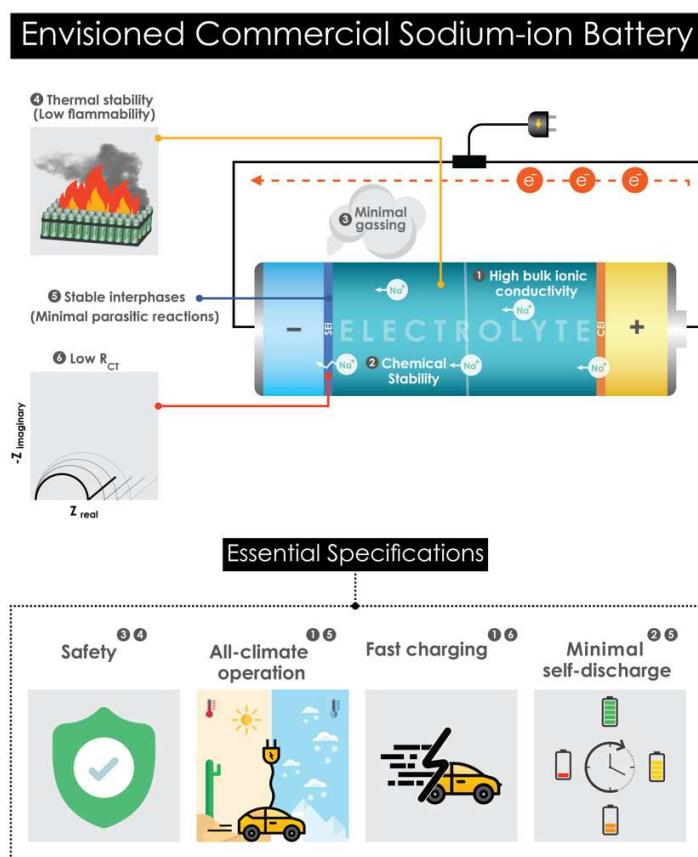
coordination for  $\text{Li}^+$  and  $\text{Na}^+$  respectively in EC solvent. (c) Histograms of the oxygen coordination number in the first solvation shell. Figures (a), (b) and (c) are reproduced with permission from [20]. Copyright © 2017, American Chemical Society. (d and e) CVs obtained in d) NP30 and e) LP30 electrolytes using a glassy carbon disk working electrode. The potential of the reference electrode ( $\text{Ag}/\text{Ag}^+$ ) is converted to  $\text{Na}^+/\text{Na}^0$  or  $\text{Li}^+/\text{Li}^0$  depending on the measured open circuit potential (OCP) of the reference electrode versus Na or Li metal. The scan rate used for CV experiments is 0.1 V/s in both electrolytes.

A glassy carbon disk electrode was used as a single working electrode material to study the electrochemical behavior of Li- and Na- based electrolytes in response to applied reductive potentials. A platinum grid and a non-aqueous  $\text{Ag}/\text{Ag}^+$  (silver wire immersed in  $\text{CH}_3\text{CN}$  containing 0.1 M  $\text{TBAClO}_4$  and 0.01M  $\text{AgNO}_3$ ) electrodes were used as a counter and a reference electrode, respectively. Figure 1d and e shows the CVs obtained in LP30 and NP30 electrolytes. A distinct electrochemical response with the appearance of a pronounced cathodic peak at *ca.* 1.2 V vs  $\text{Li}^+/\text{Li}^0$  in the CV recorded in LP30 (Figure 1d). On contrary the CV obtained in NP30 remained featureless (Figure 1e). The irreversible reduction peak observed in the CV of LP30 is attributed to the reductive decomposition of EC molecules while the absence of peak for the CV recorded in NP30 suggests an unfavored reduction process of EC in this medium.

We postulate that the high point charge effect of  $\text{Li}^+$  together with its associated four coordinating solvent molecules leads to electron deficient EC as explained above, contributing to sufficiently lowering its lowest unoccupied molecular orbital (LUMO). As a result, it becomes eventually easier for the coordinating EC molecule to accept an electron and therefore the electrochemical reduction takes place at lower overpotentials. On the other hand, the lower charge density of  $\text{Na}^+$  and the higher number of coordinating EC molecules, the LUMO of the latter are not sufficiently lowered in a way that allows it to be reduced at as low overpotentials as in LP30. It is important here to emphasize that the above discussion does not imply that EC is not reduced on the anode in NIBs, but that it takes place to a rather lower extent than it does in Li-ion counterparts and this could contribute to the observed difference in stabilities of the SEIs in both battery types. Consequently, the SEI in NIBs differ in their formation mechanism, hence at the level of composition and structure to that of SEI in LIBs. Moreover, the SEI made of Na-based salts is more soluble and poorly stable therefore affecting its global behavior as a protective layer.

#### **4. Necessity of stable interphases towards commercialization of NIBs.**

A stable SEI and CEI is essential in order to have long cycle life with good capacity retention. Apart from this, the nature and stability of SEI/ CEI also controls the essential properties such as thermal stability, safety etc. (Scheme. 1) which are extremely crucial for real-life applications of the envisioned commercial NIBs. The availability of all these specifications in the electrolyte is indispensable for enabling real-life applications of the battery.



**Scheme 1.** Schematic representation of the crucial role of the electrolyte in securing the essential specifications for commercial NIBs. The number in essential specifications correlates the corresponding property of the electrolyte with that specification.

#### 4. 1. Thermal stability

Thermal stability, which is linked to safety, is the most essential requirement for the battery for not to put end users at risk. In real-life applications, there are possible mishandling conditions in which the battery can undergo thermal (e.g. fire, overheat), mechanical (e.g. crushing of battery)

or electrochemical abuse (e.g. over charge/ discharge, short circuit etc.) that lead to rise in temperature of the battery. When the cell temperature rises beyond specific temperatures (eg. 90 °C), the interphases (SEI/ CEI) which are reported to consist of stable and metastable components could undergo exothermic decomposition, possibly generating flammable bi-products.<sup>[29]</sup> This could promote vigorous decomposition reaction between the bare electrodes and the electrolyte leading to burning of the electrolyte and thermal runaway.

High thermal stability of the electrolyte means that it is resistant against catching fire even during such exothermic parasitic reactions and over a wide range of temperature. So, nowadays more research is dedicated to the development of safer batteries by moving from organic to aqueous electrolytes,<sup>[30][31]</sup> polymer electrolytes<sup>[32][33]</sup> or even to solid-state electrolytes.<sup>[34][35]</sup> However, practical difficulties in using these electrolytes in commercial batteries are much higher and the readers are directed to specific reviews on these topics.<sup>[34][36]</sup> Unfortunately, the overwhelming majority of the alkali metal-ion batteries (LIBs and NIBs) at present employ liquid electrolytes based on organic solvents (esters and/or ethers), consequently the absolute thermal stability cannot be attained.

So, at present, the safety of the commercial batteries against explosions/ firing is achieved using safety devices such as a thermal fuse, positive thermal coefficient (PTC) or current interrupt devices (CID).<sup>[8]</sup> The PTC exhibits low resistance at usual operating conditions and the resistance increases to shut the current flowing to the battery when the battery temperature rises beyond the safety limit. The process is reversible as the PTC resistance decreases again to make the cell work usually when the normal operating conditions are recovered.<sup>[37]</sup> However, CID is a fuse type device and it shuts the current permanently during high pressure, temperature, or high voltage. The LIBs are additionally protected using a safety vent which opens up and release the evolved gas to decrease the cell pressure, when PTC/ CID fails to provide protection.

In purpose of reducing the use of such sophisticated safety devices in the batteries, more research is being devoted to study additives that improve the thermal stability of SEI/ CEI and/or “unusual” solvents such as trimethyl phosphate (TMP) that demonstrate fire retardant properties.<sup>[38]</sup> TMP is used in paint industries as fire retardant since their gaseous form, on sudden heating breaks into phosphorous-containing radicals that scavenges the H<sup>•</sup> radicals that are the

major cause of fire.<sup>[39]</sup> The same mechanism of fire retarding is expected to apply when TMP is used as an electrolyte component in batteries. However, further studies are still needed in order to come up with a conclusion concerning the viability of TMP-based electrolytes in satisfying the other requirements.

#### **4.2. Ability to work in different climatic conditions, cycle life of the battery**

If commercialized, NIBs are required to sustain all climatic conditions by maintaining good cycle life as well as power performances. The primary requirement for the ability to operate in all climatic conditions is the good bulk Na<sup>+</sup>-ion conductivity in the electrolyte. In fact, this is the first property that must be considered and measured during the electrolyte design. Once this is met, the electrolyte is selected based on their boiling and crystallization temperature to know the temperature window within which the electrolyte remains in its liquid form to ensure good battery performance. In addition to the bulk Na<sup>+</sup>-ion conductivity, the charge transfer resistance also needs to be minimal for achieving high power performance. The CEI/ SEI also leads to increase in resistance and hence reduce the power performance. Especially, the thickness of CEI/ SEI depends on the temperature at which the cell cycles. Hence, the stability and charge transfer resistance of the SEI/ CEI is important to guarantee proper functioning of batteries irrespective of the cycling temperatures.

If the SEI is not stable at high temperatures, the unwanted parasitic reactions are promoted within the battery, leading to the gradual depletion of the electrolyte and eventually to cell failure.<sup>[40]</sup> The decomposition reactions could generate gaseous products that lead to pressure build-up inside the cell thereby increasing the risk of an explosion. Further, the electrolyte decomposition may also generate a thick SEI of large impedance that leads to cell heating and eventually a thermal run away. This implies a short cycle-life with increased safety issues especially in extreme working conditions. On the other hand, at low temperatures the ionic conductivity could decrease dramatically leading to high polarization and possible Na plating on the electrode, hence a detrimental deterioration in the charging/discharging performance of the battery. This is the reason, the cyclic propylene carbonate (PC) is introduced as co-solvent in LIB electrolytes and is found to extend the freezing temperature of the electrolyte and also helps in forming SEI with improved charge transfer properties.<sup>[41]</sup>

### **4.3. Low self-discharge.**

Self-discharge is the phenomenon during which the cell loses its capacity while it is at rest.<sup>[42]</sup> It can be reversible as is the case of Ni-MH batteries or irreversible where the lost capacity cannot be recovered by re-charging the cell. A typical Li-ion battery self-discharges about 5% in one day and 1-2 % per month at room temperature and normal operating conditions.<sup>[42]</sup> Such low self-discharge rate adds advantage to the LIB technology. However, the self-discharge rate could increase with temperature or under extreme voltage conditions. Considering NIBs, since the formed SEI/ CEI is not stable under a given condition, side reactions are aggravated within the cell leading to irreversible capacity loss.<sup>[43]</sup> Further, NIBs are usually advertised for their ability to be stored and transported at 0 V which is the extreme voltage condition,<sup>[44][3]</sup> thus the stability of SEI/ CEI at 0 V storage need to be addressed.

## **5. How to improve the interphase stability: The role of electrolyte additives**

Obviously, there is an essential need to optimize electrolyte formulations for NIBs in order to come up with a suitable electrolyte recipe that is able to provide an SEI with ideal properties. As the solvent/salt components alone have proved their incapability of achieving that, doping the electrolyte with additives becomes the best strategy to circumvent this restriction in NIBs. Additives are chemicals that are added in small quantities (typically between 1 and 5% w/w) into the mother electrolyte mixture in order to promote or even impart it one or more desired properties that could be weak or missing in the pristine electrolyte. Such properties could be: increased wettability, safety (decreased flammability),<sup>[45]</sup> chemical stability and film forming capability<sup>[46][43]</sup> etc... In NIBs, most of the research in additives is focused on its enhanced film forming ability since the NIBs lack robust interphases. In such case, the additives are expected to reduce (for SEI) or oxidize (for CEI) before the onset of the solvent decomposition, thereby participating in the SEI/ CEI formation and substantially changing their properties in comparison to those derived from additive-free electrolytes.

### **5.1. Film forming additives reported for NIB electrolytes**

Several film forming additives, known in the LIB field, have been revisited and studied for NIBs. Remarkably, the majority of these additives are fluorine-based due to the superior passivation ability demonstrated by these compounds through the generation of sodium fluoride NaF which is

considered as a crucial component of a robust SEI. Among these additives are fluoroethylenecarbonate (FEC),<sup>[47]</sup> difluoroethylenecarbonate (DFEC), fluorinated dimethylcarbonate (DMCF),<sup>[48]</sup> sodium oxalate difluoro borate (NaODFB) etc, with the expectations to form SEI consisting of NaF and be more stable upon cycling and during self-discharge. Komaba et al. reported stable SEI with FEC additives in Na-metal cells using  $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  positive electrode.<sup>[47]</sup> However, the studies from R. Dugas et al. claim that the stabilization effect of FEC is associated with the Na-metal counter electrode and is not present when Na-ion full cells with hard carbon negative electrodes are used.<sup>[49]</sup> This shows the importance of the electrode material in determining the SEI chemistry and the necessity of carrying out the studies in Na-ion full cells in order to come up with decisive conclusions. NaODFB is explored as effective electrolyte salt<sup>[19]</sup> as well as an additive to form stable SEI.<sup>[50]</sup> However, increasing the NaODFB additive beyond the specific limit is reported to rise the cell resistance leading to cell failure.<sup>[43]</sup> Other additives such as organic carbonates that reported to polymerize and form stable SEI/ CEI (e.g. Vinylene carbonate, vinyl ethylene carbonate)<sup>[51]</sup> and sulfur containing additives (e.g. 1,3- propane sultone), have also been studied for NIB electrolytes.<sup>[43]</sup>

As implied above, most of the studies on the additives are carried out in Na-metal half cells except very few studies in Na-ion full cells where issues from the positive electrode were observed. These problems from the positive electrode in NIBs are more pronounced when  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$  or sodium layered oxides are used as positive electrodes, since most of their capacity is attained by cycling the material to high voltage.<sup>[52][53]</sup> For example, the  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$  exhibit a long plateau at 4.2 V from which 50% of their capacity is realized. Similarly, sodium layered oxides could be useful only if the full capacity is utilized (> 80%) which involves the oxidation process above 4 V.<sup>[54]</sup> Nevertheless, high energy of the battery could only be achieved with high capacity and voltage explaining the importance of having effective protective layer on the positive electrode as well.

To protect the positive electrode, the additive such as adiponitrile,<sup>[55]</sup> N-Propyl-N-Methyl Pyrrolidinium bis(trifluoromethanesulfonyl)imide,<sup>[56]</sup> trimethylsilylphosphate, tris(trimethylsilyl)phosphite<sup>[57]</sup> etc were investigated. They can be used by combining with additional additive(s) to protect the negative electrode (e.g. NaODFB).<sup>[28][43]</sup> So, using a blend of

additives that work in synergy is now a preferred approach to achieve the protection of both positive and negative electrodes.<sup>[55][43][28][46]</sup> However, considering the accumulated empirical knowledge throughout the years of research on electrolyte additives for LIB electrolytes, it is not a simple process to study and screen all possible additives for NIB electrolytes. Further, due to the difference in Li and Na-ion chemistries, the efficient additives used in LIBs would not necessarily be efficient if used in NIBs. Essentially, new additive blends should be developed and tuned if this technology is to be upgraded and fast screening methods need to be introduced for selection of suitable additive(s).

## 5.2. Fast screening of additives by CV

Screening electrolytes following the common methodology generally requires a long time of cell cycling and analyses in order to come up with conclusion concerning the role of each of the electrolyte components (solvent-salt-additives). Thus, there is a compelling urge to find an alternative way to accelerate these tests. The development of high throughput approaches for screening the best additives is rapidly developing but success is still limited. Meanwhile, we identified that CV could be a fast and a useful tool for the preliminary assessment of the SEI-forming capability of the electrolyte including the additives. Along this line, we have utilized CV in the presence of glassy carbon working electrode as a model for the carbonaceous electrodes hard carbon (HC) and graphite in NIBs and LIBs respectively, in order to investigate not only the awaited formation of SEI upon imposing reductive potentials, but also its stability (durability).<sup>[28]</sup> The idea is based on mimicking the events taking place at the negative electrode within an operating battery, where the potential drops gradually and slowly during charging provoking the electrochemical decomposition of the electrolyte components leading to the formation of the SEI. Although relatively faster than the events in a real battery, the CV experiment could give a reliable anticipation of the behavior of the electrolyte in terms of SEI formation, stability and consequently of the global performance of the cell (Figure 2c-d). The advantage of such an experimental setup is that it enables acquiring real-time information about the system and thus assisting in faster screening of electrolyte formulations.

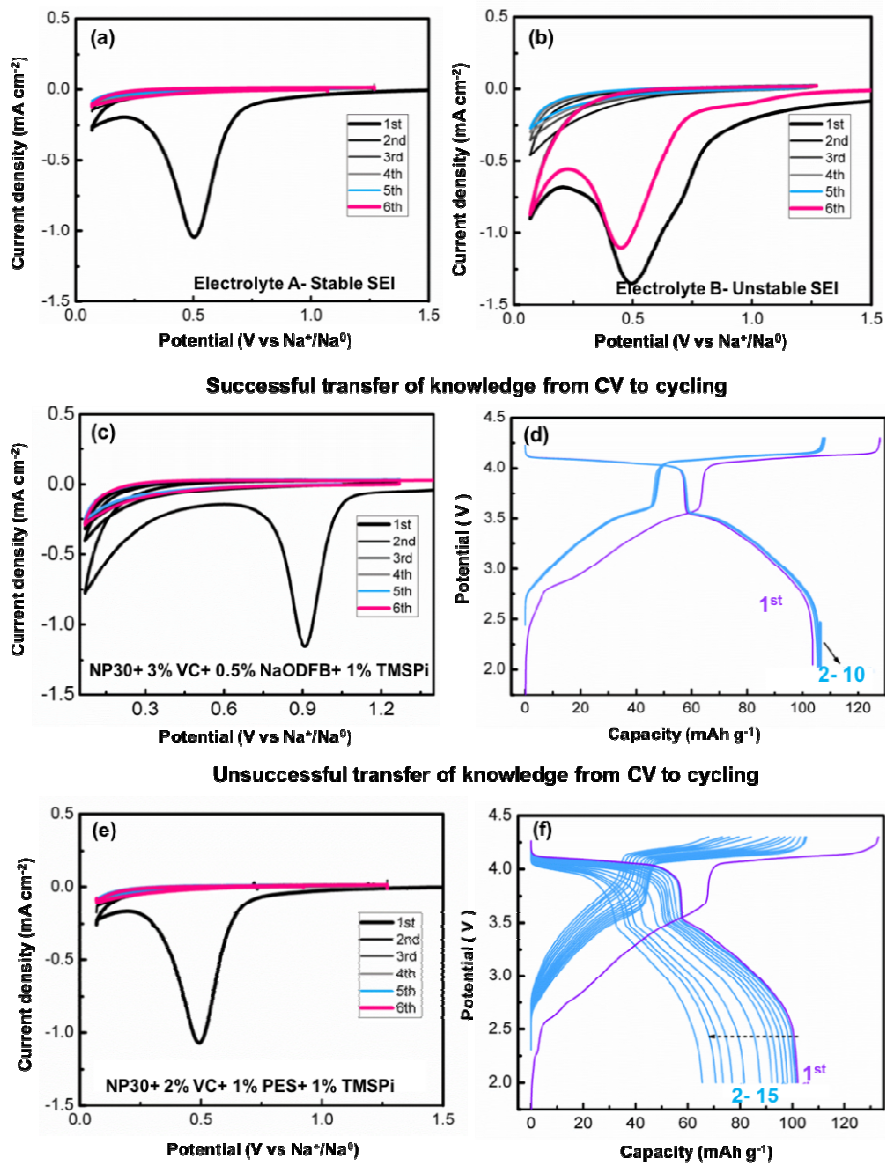
In a typical measurement, the GC electrode is driven to lower potentials very close to 0 V vs Na/Na<sup>+</sup> in the electrolyte in question. The electrolyte hosting one or several additives which



could be electrochemically active and their reductive potentials are expected to be within the potential window of study, i.e.  $> 0$  V vs.  $\text{Na}^+/\text{Na}^0$ . How does it work? Let's suppose that we have two electrolyte formulations: Electrolyte A and Electrolyte B containing different additives X and Y respectively. Five successive CV scans are recorded in both electrolytes then a resting time  $t$  ( $t$  could typically be any value  $< 1$  hour) at open circuit potential (OCP) is allowed before a 6<sup>th</sup> scan is recorded. Following the first scan that features a distinct irreversible process attributed to the reductive decomposition of additives, the consecutive scans demonstrate a massive suppression of Faradaic current. Such a behavior is attributed to the insulation of the electrode surface due to the adsorption of an insulating layer (basically the SEI) resulting from the electrochemical reductive decomposition. Now that the SEI is formed onto the electrode surface, testing its stability remains the critical step before the final judgement on the electrolyte. If the 6<sup>th</sup> CV recorded after a resting time  $t$  at OCP is identical or similar to the 5<sup>th</sup> one recorded before resting this means that the SEI is stable as it remained adhered to the electrode surface and was still able to suppress the heterogeneous electron transfer from the electrode towards the solution (See Electrolyte A in [figure 2a](#)). On the contrary, if the 6<sup>th</sup> CV scan features an important Faradaic current i.e. it resembles the 1<sup>st</sup> recorded CV, this indicates that the formed SEI was fragile as it didn't sustain for a long time at OCP and it was either detached or dissolved (see the case in Electrolyte B, [figure 2b](#)). Once the good electrolyte is identified, it must be tested in a real battery to confirm its positive attributes. Finally, it is worth mentioning that it is important to carry this test at different temperatures to have a more reliable judgement on the electrolyte performance since its behavior could improve or deteriorate at different conditions depending on the electrolyte composition.

The experiment helps us to quickly screen the electrolyte additives and follow their roles during SEI formation. Similar experiments could be performed using more realistic conditions such as using a hard carbon electrode instead of glassy carbon. Although such CV experiments could provide a rough idea of the expected SEI stability, they differ in the time scale when compared to the real batteries and are also incapable of providing deeper revelations concerning SEI properties (example shown in [Figure 2e-f](#)). For example, if the formed SEI grows thick and/or exhibit high impedance upon cycling, it cannot be visualized from CV experiments alone. Thus, additional tools such as electrochemical impedance spectroscopy (EIS) which could provide information

about the resistive nature of SEI/ CEI with time could be coupled with the CV experiments. Although CV could be a useful technique that helps in a preliminary assessment of the electrolyte components, further testing in actual full battery cells are essential in order to draw out solid conclusions.



**Figure 2.** (a, b) Model cyclic voltammograms to describe the identification of (a) stable SEI, and (b) poorly stable SEI by CV. (c and d) A representative example for successful implementation of CV for additive selection. NP30 with additives vinylene carbonate (VC), sodium-oxalatedifluoroborate (NaODFB) and tris-trimethylsilylphosphite (TMSPi) exhibited stable SEI in CV and stable cycling performance while testing in coin cells. (e and f) A representative example where stable SEI is observed in CV but deterioration in cycling performance was observed (electrolyte used was NP30 with additives VC, prop-1-ene-1,3 sultone (PES) and TMSPi). Both the cycling profiles shown here are derived from coin

cells using  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$  and Hard carbon as positive and negative electrodes, and the experiments are carried out at 55 °C. The cells are cycled at C/5 (1C= 120 mAh g<sup>-1</sup>).

## 6. Experimental techniques to screen the electrolyte salt(s), solvent(s) and additive(s)

In order to test and compare new electrolyte formulations and to identify their suitability for real-life applications, it is vital to set experimental protocols that take into consideration all the required specifications. This could help bridge the gap between the acquired knowledge at the laboratory scale and the ability to exploit this knowledge in developing battery devices that fulfill the commercial standards. In the following subsections, we explain a simple experimental protocol that can be used at the laboratory scale to quickly screen new electrolyte formulations. It should be mentioned that the more detailed studies aiming to gain a deeper understanding of the nature/ composition/ morphology of the interphases are not reviewed here.

### 6.1. Ionic conductivity/ viscosity and separator wettability.

The Na-ion conductivity of the electrolyte is the primary and most important parameter that must be considered in the selection of an electrolyte. Each electrolyte component, whether it is the solvent, the supporting salt or the additives if any, all play a role in determining the ionic conductivity of the final electrolyte. Preliminary selection of solvents and salt concentrations can be done based on the reported values of ionic conductivity for different solvent mixtures. However, it is essential to experimentally measure the ionic conductivity of the final electrolyte. The bulk ion conductivity ( $\sigma$ ), which is the ability of ion conduction in the solution, is usually measured in lab by an adapted instrument called conductivity meter and the expected value is around 10 mS cm<sup>-1</sup> at 25 °C. Since, the ionic conductivity varies as a function of temperature, it is necessary to measure the conductivity at different temperatures and the electrolyte with optimum conductivities at all temperatures is preferred over electrolytes that show maximum conductivity exclusively at room temperature. [Figure 3a](#) shows one such example of ionic conductivity measurements of  $\text{NaClO}_4/\text{NaTFSI}$  in different solvent mixtures together with the change in conductivity as a function of temperature ([Figure 3b](#)).

It is worth mentioning that the measured ionic conductivity represents the overall conductivity resulting from the contribution of both cation and anion of the salt. In a metal-ion battery, only the contribution of the cation is what matters and thus to discriminate between the contribution of

each of the ions to the overall conductivity, another descriptor is put in place, the transference number ( $t$ ). Transference number is the fraction of ionic current carried out by the positive ( $\text{Na}^+$ ) or the negative ion (e.g.  $\text{PF}_6^-$  in  $\text{NaPF}_6$ ) in the electrolyte, with the total being 1. In some cases, low transference number of cation or high current contribution from anions can cause concentration polarization that is detrimental for dendrite growth. In conventional carbonate based liquid electrolytes, the large solvation shell of the solvent molecules around  $\text{Na}^+$ , yield a low cation transference number (typically 0.2- 0.4), implying a significant contribution of the anion to the global ionic conductivity. The transference number and the transport properties of the cation and anion could be analyzed using electrochemical methods and/or nuclear magnetic resonance (NMR) measurements.<sup>[58]</sup> However, the method is not employed in routine analyses for optimization purposes. Instead, a preliminary knowledge from previous studies are used to select the proper electrolyte formulation.

Besides ionic conductivity, the other parameters such as viscosity and wettability are also considered for the initial screening of electrolytes. Highly viscous electrolytes reduce ionic conductivity (Figure 3a) and suffer from a weak wetting ability towards the separator. Hence, low-viscosity solvents such as linear carbonates are often used in order to reduce the overall viscosity of the final electrolyte. Viscosity can be measured using viscometer while wettability is estimated directly using contact angle measurements. Small contact angle values are associated with the high wettability. It is to be noted here that although the wettability is related to the viscosity of the solvent, it also depends on the interaction between the electrolyte in its entirety and the separator. Therefore, the wettability of a given electrolyte salt and solvent(s) can be affected if additives are used.

The initial assessment of an electrolyte is carried out by investigating its ionic conductivity and electrochemical stability. If the electrolyte demonstrates an acceptable behavior at the level of these parameters, they are then subject to testing their ability of forming a stable SEI. The latter study is carried out by following the electrochemical performance of the Na-ion cells involving the electrolyte in question. In parallel, it is essential to analyze the occurrence of unwanted side reactions and probable gas evolution during cycling. Finally, all the previous tests are followed by post mortem analyses of the cell components in order to gain a deeper insight on the global

cell status such as the SEI/ CEI composition, metal dissolution, current collector corrosion, metal plating etc.

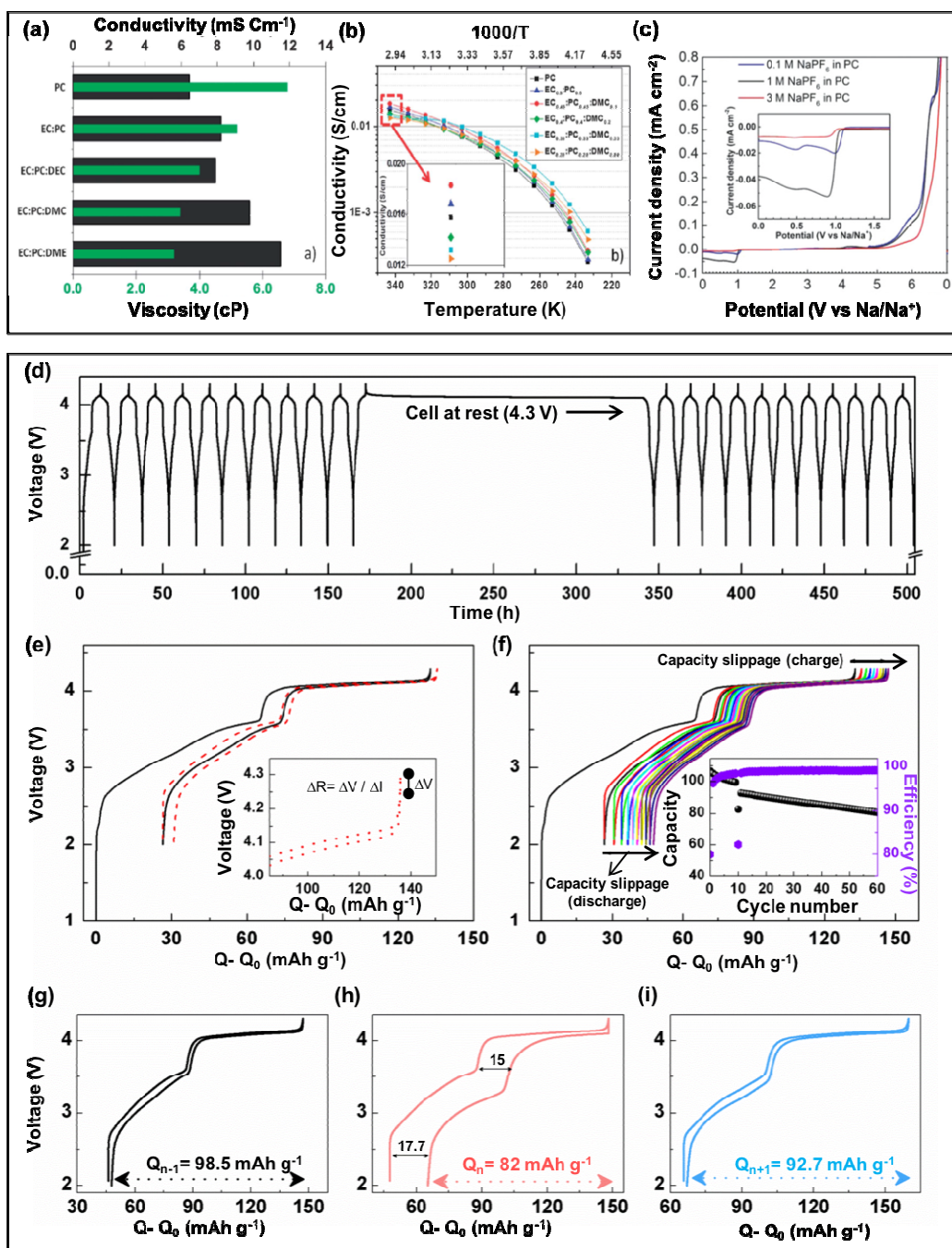
## **6.2. Analyses on electrochemical performance of the electrolytes.**

Testing the electrochemical stability of the electrolyte is usually carried out using Linear Sweep Voltammetry (LSV) experiments (Figure 3c) or CV experiments. However, as discussed above, the electrolyte components decompose on the electrode surface to form the SEI/CEI thereby kinetically extending its electrochemical stability window. Accordingly, a more reliable analysis of the electrochemical stability window should be performed in a full cell in presence of the two concerned electrode materials. For this purpose, coin- or pouch- type cells are mounted and their electrochemical stability window together with the tests on their performance are carried out using either constant voltage or constant current techniques. One of the essential points here is to have electrodes as standards such that electrodes which are properly coated and calendared are used for comparing the performances of different electrolytes in order to exactly mimic the electrode surface reactions that are possible in real-life batteries.

As a case study, we discuss the electrochemical analyses of the NP30 electrolyte that we carried out in NVPF/HC coin type 2032 full cells. To prepare the electrode films, each of the HC and NVPF materials were mixed with conducting carbon, and polyvinylidene difluoride (PVdF) additive, then the slurry was cast on aluminum foil. The porosity of the electrodes after calendaring was 35 and 40 % respectively for the positive and negative electrodes respectively. The mass loading of the electrodes are done such that the positive to negative electrode mass ratio is 2:1 to match the practical capacities. The electrodes were punched into circular discs of 13 mm diameter and assembled in coin type 2032 cells. The electrochemical performances are analyzed using biologic cyclers and the results are compiled in Figure 3(d-i).

Figure 3d shows the galvanostatic (constant current) charge/ discharge cycles of the cell where the experiment was performed at a fixed temperature of 55 °C to accelerate the parasitic reactions for quick analysis. The total delivered current during the time of the charge or discharge was used to calculate the practical capacity of the cell. The cycling profile by plotting as shown in Figure 3e provides information about the polarization of the cell. Any change in the impedance upon cycling can be followed by consecutive EIS measurements as the cell cycles. Alternatively, the





**Figure 3.** (a) Ionic conductivity values (mentioned as black bars) of 1M NaClO<sub>4</sub> in different organic solvent(s) with the viscosity in green bars. (b) Arrhenius plots of conductivity (as a function of temperature) of the electrolyte 1 M NaTFSI salt dissolved in different solvent(s) (reproduced with the permission from <sup>[52]</sup>); Copyright 2013, Royal Society of Chemistry. (c) Electrochemical stability window obtained using LSV in three electrode cells with different concentrations of NaPF<sub>6</sub>. Reproduced with permission from <sup>[59]</sup>; (License number 4947141028858, copyright from John Wiley and Sons). (d) Galvanostatic charge-discharge cycles of the NVPF/hard carbon electrode cycled in NP30 electrolyte at

55 °C in coin cell mode. (e) The voltage versus differential capacity plot of the data shown in 'd' with the inset showing the zoomed image to visualize polarization. The apparent resistance is calculated by dividing the change in voltage for the given change in current at particular time interval ( $\Delta t$ ). (f) First 10 cycles showing the slippage in capacity on charge and discharge with the inset showing the capacity retention plot and the efficiency during cycling. (g-i) The analyses on self-discharge experiments where the cycle before self-discharge is shown in (g) and the charge for self-discharge and subsequent discharge after 168 h rest at 4.3 V shown in (h) and the recovery cycle in (i). In the given example, 83 % capacity is retained after 168 h self-discharge at 4.3 V and the recovery is 94% of the cycle before self-discharge.

apparent resistance ( $\Delta R$ ) could be also calculated from the cycling profile itself (inset in Figure 3e).<sup>[43]</sup> By following the change of this quantity upon cycling we could gain a direct insight on the resistance evolution. Continuous increase in resistance and polarization is a direct indication of the cell failure. The cycling profiles when superimposed together as in Figure 3f and information on the capacity slippage on charge and discharge could be acquired. These capacity slippage values could be calculated as explained by Dahn et al.<sup>[60]</sup> However, such calculations are meaningful only when high accuracy coulometer is used in addition to the use of cells with high amount of active material (such as pouch/ cylindrical/ rectangular types) that ensures the high flow of current for testing and relatively less error in measurements. For coin cell studies in the laboratory, such accurate calculation is not facile; however, a comparative study can be done by following the charge/ discharge slippage. Furthermore, by following the capacity retention and coulombic efficiency, the capacity decay indicates degradation in electrode material and/or increase in cell impedance, whereas a coulombic efficiency inferior to 100% is an indication of parasitic reactions taking place in the electrolyte (inset in Figure 3f).

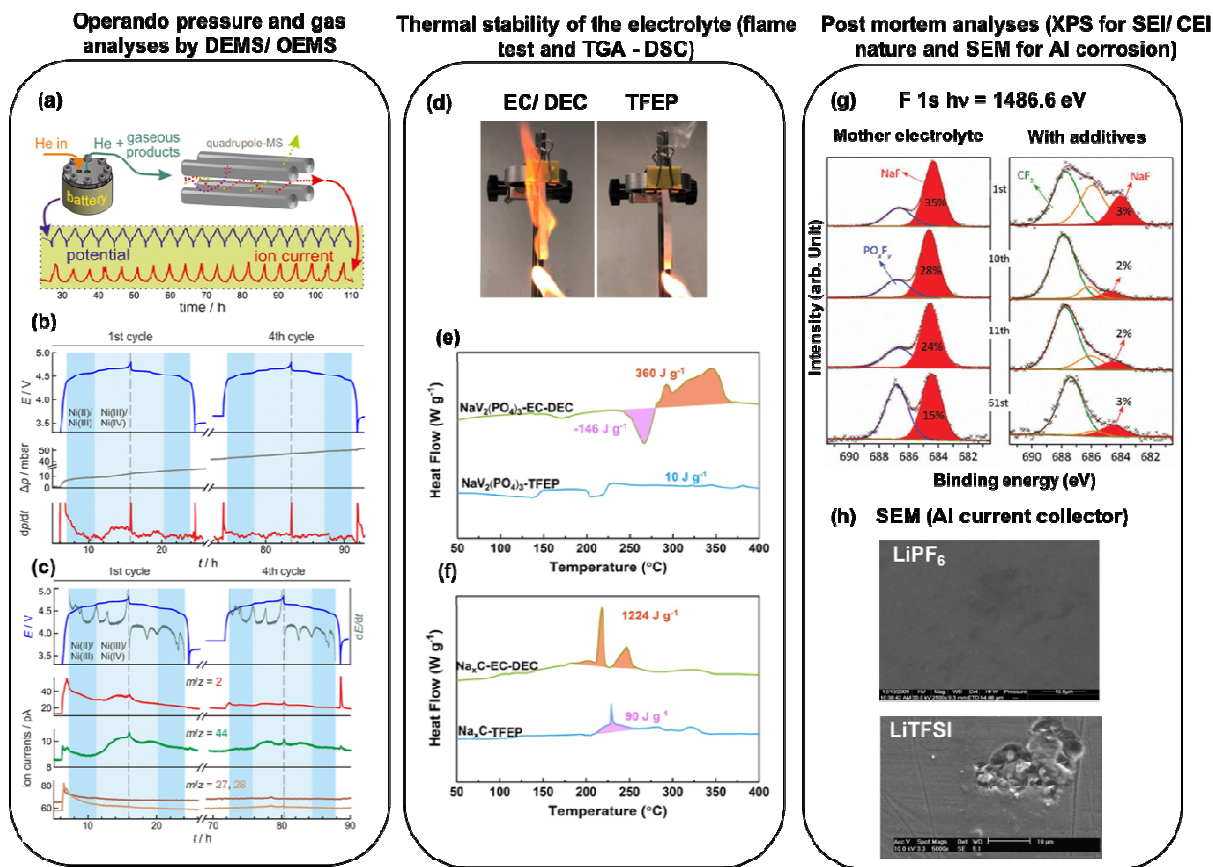
In order to evaluate the stability of the interphases in the battery, it is ideal to follow its self-discharge behavior that is closely related to the side reactions that would take place at the electrodes if the SEI or CEI are fragile. These tests are performed here at 55 °C by holding and already cycled cell at its full state of charge (SOC) i.e. at 4.3 V after the removal of 2 Na from NVPF for a given period of time (1 week in this particular experiment) and then allowing it to continue cycling under the same conditions (Figure 3g- i). Holding the cell at 100 % SOC and at 55°C aims to impose the extreme conditions at which side reactions are promoted and self-discharge would be maximal. The first discharge after the resting period (1 week in this particular experiment) is characterized by its capacity ( $Q_n$ ) which when compared with the corresponding charge capacity (i.e. just before holding) provides information about the extent of self-discharge that took place during the holding period. Furthermore, the ratio of the discharge capacity of the

subsequent cycle ( $Q_{n+1}$ ) to that of the last cycle before resting ( $Q_{n-1}$ ) is taken as an index of the recovery ability of the battery after being subject to extreme (1 week at 4.3 V, 55 °C) conditions favoring the self-discharge. If the used electrolyte possesses all the requirements discussed above the self-discharge would be minimal, and 100 % recovery ( $Q_{n+1}/Q_{n-1}=1$ ) is expected.

### **6.3. Analysis of gas evolutions and pressure changes**

Thermal stability and safety of the battery is the most important phenomenon to be well understood before commercialization of the battery. However, the alkali metal-ion batteries are known to heat up during cycling thus triggering parasitic reactions within the electrolyte that are often associated with the formation of gaseous products. Even worse, certain additives, could continuously produce gaseous products when they react with the other electrolyte components, thus compromising the important safety requirement of the battery. In order to better understand the gassing phenomenon in the battery and its origins in the electrolyte, it is essential to examine the nature and quantity of the produced gases. In coin cells, such gas evolution is not directly detectable since the produced gas could occupy the empty space available within the cell. On the contrary, this phenomenon is easily detectable in pouch-type cells where the swelling is observed. The quantity of the evolved gas is estimated by measuring the weight of the pouch cell before and after cycling. This experiment provides information on the quantity and not on the identity of the evolved gases. However, unraveling the identity of evolved gases is essential especially when these gases could be reactive with the cell components. For this purpose, online electrochemical mass spectrometry (OEMS) or differential electrochemical mass spectrometry (DEMS) is used and the gas evolved from the cell is collected and analyzed by mass spectrometry. The gas collection could be done simultaneously during cell cycling or by degassing an already cycled cell. By calibrating the gases and the signal for different gases, quantification of the evolved gases can be done. These experiments could be performed at different temperatures and the data from different electrolytes could be easily compared and analyzed. The DEMS/ OEMS analyses have been extensively used to study the LIBs electrolytes and a representative example is shown in [Figure 4a-c](#).<sup>[61][62]</sup> However similar studies with NIBs electrolytes are relatively less except in few studies that aimed to investigate O<sub>2</sub> evolution from the electrode material in half cell mode.





**Figure 4. (a- f)** Analyses on change in pressure, thermal stability and safety. (a) A representative cell model used for following the online pressure changes using DEMS measurement for long cycling. (b and c) A pressure analyses done on  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ / graphite based Li-ion cell where the change in pressure is mentioned as  $\Delta P$ , the mass spectra for the molecules  $\text{H}_2$  ( $m/Z=2$ ),  $\text{CO}_2$  ( $m/Z=44$ ) and ethylene  $\text{C}_2\text{H}_4$  ( $m/Z=27, 28$ ) are shown in (c), (reproduced with permission from <sup>[62]</sup> and <sup>[61]</sup> for (a) and (b,c) respectively; Copyright © 2015 American Chemical Society). (d) Flame test showing the high flammability and better thermal stability of EC/ DEC based electrolyte with and without TFEP additive, respectively. The thermal stability of both electrolytes are also compared using DSC analysis (e) in presence of desodiated  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  positive electrode and (f) sodiated carbon negative electrode (reproduced with permission from <sup>[45]</sup>; copyright 2018 © Elsevier). (g and h) post mortem analyses, (g) F 1s XPS data of 1M  $\text{NaPF}_6$  in EC-PC (mother electrolyte), and with additives (VC, NaODFB, succinonitrile (SN) and 1,3- propane sultone (PS)), reproduced with permission from <sup>[43]</sup>; copyright from John Wiley and Sons. (h) Scanning electron microscopic (SEM) image of Al current collector after cycling when the cell cycled with electrolyte containing  $\text{PF}_6^-$  and TFSI salts of Lithium. Al corrosion was observed with LiTFSI but no corrosion seen with  $\text{LiPF}_6$  based electrolytes, reproduced with permission from <sup>[63]</sup>; copyright Elsevier.

Although of crucial importance is in-live monitoring of the SEI during its formation and its associated thermal and pressure effects. Optical sensing was recently shown as an elegant method to monitor such changes.<sup>[64]</sup> To do so, Fiber Bragg Grating (FBG's) sensors were injected into a 18650 Na-ion cells with the shift in the FBG signal, that is a function of T, P and strain ( $\epsilon$ ), being

monitored as a function of cycling and else. Thus the authors could access the pressure build-up and heat generation of NP30 electrolyte upon various testing protocols. The results provide clear evidence on the huge gas evolution in Na-ion electrolytes. Sensing the events within the battery using optical sensors is possible for hundreds of cycles thus providing long cycling analyses. However, the usage of optical sensors and the related sensing methodology cannot be used as routine analysis technique due to its complexity and limited availability of the needed instrumentations, in addition to the requirement of 18650 or pouch type cells with large mass of the active materials. Hence, devising sensing methods that are adapted to coin cells scale would be more useful for routine analysis.

#### **6.4. Thermal stability of the electrolyte**

The absolute thermal stability of the electrolyte is often proved using flame test where the separator is soaked with the electrolyte under study and introduced directly to the flame. Such experiment could be used where absolute thermal stability is expected and the electrolyte does not catch fire. The [Figure 4d](#) shows an example of such experiment. Since TFEP, a flame-retardant additive, was added to the electrolyte, the flammability of studied electrolyte is suppressed.<sup>[45]</sup> However, the organic carbonate based liquid electrolytes without any flame-retardant additives does not exhibit absolute thermal stability. Still, it is essential to know the flash point of the electrolyte and the amount of heat that could be released when the electrolyte burns. The fire incident would be more severe if the contact between the electrolyte and electrode material releases oxygen/ hydrogen during the fire. So, it is essential to study the thermal stability of the electrolyte in presence of the electrode in its highly charged/ discharged states. Thermal gravimetric analysis (TGA) and differential calorimetry (DSC) are ideally used to understand the thermal stability of electrolyte. The simultaneous TGA-DSC analysis could be carried out for the electrolyte separately or in presence of the electrode material in its highly charged/discharged state in order to simulate the actual conditions in a battery where electrodes are present ([Figure 4e,f](#)). The experiments are performed in an argon atmosphere and the electrolyte decomposition is measured as function of temperature. The heat evolution could be quantified and compared for different electrolytes. [Figure 4e,f](#) shows the TGA of two different Na-ion electrolytes in presence of de-sodiated  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  and sodiated hard carbon respectively.

### **6.5. Nature of SEI/ CEI: *Operando* / *ex-situ* (post mortem) techniques.**

Even after 25 years of research in LIBs towards understanding the SEI/ CEI, very less is understood so far and attaining complete knowledge on interfacial reactions that happen within nanoscale regions is very difficult. Several *operando* and *ex-situ* techniques are developed to follow the interfacial reactions and the subsequent formation of interphases.<sup>[65][66][67]</sup> This includes infrared spectroscopy,<sup>[68]</sup> Raman spectroscopy,<sup>[69]</sup> ultra violet spectroscopy and several electroanalytical techniques etc.<sup>[70]</sup> The morphology of the interphases is often followed by microscopic analysis and the rigidity/mechanical strength is analyzed by EQCM.<sup>[71]</sup> Surface techniques such X-ray photo electron spectroscopy (XPS)<sup>[48][43]</sup> and time-of-flight secondary ion mass spectrometry (TOF-SIMS)<sup>[72]</sup> are highly used in electrolyte studies to identify the SEI/ CEI composition and their growth upon cycling (example for XPS data shown in [Figure 4g](#)). Several other techniques are in trial or in development stage in order to get better knowledge about the SEI/ CEI formation and its nature/ stability etc. Although routine usage of these techniques during initial screening stages of the electrolyte is not feasible, the deeper understanding of interphases is essential from time to time, for further progressing with the electrolyte optimization. Hence explaining the European initiative BATTERY 2030+ where the understanding of the interface via artificial intelligence is one of the great challenges.<sup>[73]</sup>

### **6.6. Analyses on electrolyte reactions with cell components (post-mortem analyses)**

The other important property of the electrolyte is its stability towards cell components. In order to diagnose the chemical stability of an electrolyte, the first component to investigate is the Aluminum current collectors on which the electrode materials are usually coated. Some electrolytes (e.g. electrolyte salts having TFSI anion) are known to severely corrode Al foil due to its incapability of forming a protective passivation film. The Al corrosion in a given electrolyte could be simply studied, either by voltammetry techniques prior to cell cyclic through employing an Al foil as a working electrode or by recovering the Al-current collector from the cells after cycling in order to analyze it by scanning electron microscopy ([Figure 4h](#)).

## **7. Summary and outlook**

As is the case in LIBs, conventional organic electrolyte based on sodium salts in a solvent mixture of cyclic and linear carbonates, is still the formulation of choice for NIBs. However, the

interphase (SEI and CEI) formed in case of NIBs suffer from poor stability and dissolves/ decompose upon long cycling leading to cell deterioration. The deterioration in battery performance is more pronounced at elevated temperatures and high oxidizing working potentials. To this end, the use of electrolyte additives turned out to be an important game changer. Although no single additive has proven capable alone of providing solutions for all the problems, thought-out combinations of several additives have afforded promising results for realizing a breakthrough in this deadlock. The efficiency of an additive varies with the electrodes in use, hence making the additive selection to be delicate and highly dependent on each system's conditions.

Importantly, if the additives blend provides stable SEI/CEI, this doesn't necessarily mean that the electrolyte in question is applicable for commercial batteries as other problems may show up. In our group, we have come up with two different electrolyte formulations that showed excellent electrochemical performance in terms of self-discharge and recovery even at elevated temperatures. The first formulation is based on 1M NaPF<sub>6</sub> in EC- PC with succinonitrile, vinylene carbonate, 1,3 propane sultone and sodium difluorooxalatoborate (NaODFB).<sup>[43]</sup> However the practicality of this electrolyte is limited by the usage of solely cyclic carbonates which increase the viscosity and reduce the ionic conductivity, wettability of the electrolyte. In such case, the cell design needs to be modified with separators that shows improved wetting property but it comes with other difficulties in cell assembly. Later, we have succeeded to overcome these problems through a new electrolyte formulation constituting of EC-DMC mixture with additives NaODFB, vinylene carbonate VC and tris- trimethylsilylphosphite (TMSPi). Unfortunately, one of the the used additives TMSPi exhibited detrimental reactivity that resulted in continuous gas release which lead to pressure build-up and cell failure.<sup>[28]</sup> These results underlie the importance of analyzing all essential properties together during the identification of suitable electrolyte for NIBs targeting real life applications.

Instead of conventional designs, non-conventional electrolytes were also studied for possible utilization on sodium ion batteries. Among the different non-conventional electrolytes studied so far, electrolytes based on ionic liquids as solvent take the main place due to their non-volatility, low flammability, and high chemical stability.<sup>[74]</sup> Though poor total ionic conductivity is reported with ionic liquid based electrolytes, the higher transference number for Na<sup>+</sup> in ionic liquids

offsets this drawback and good Na-ion conductivity is reported with ionic liquid based electrolytes.<sup>[75]</sup> Similarly, it was believed that the absence of molecular species result in non-formation of SEI/ CEI and hence possibility to use in combination with highly reactive electrodes as well.<sup>[76]</sup> Recently, the studies show SEI formation in ionic liquid based electrolytes by the decomposition of electrolyte salt.<sup>[16][77]</sup> The formed SEI is thermally stable and also show high resistance to Al corrosion, hence allowing the use of ionic liquid based electrolyte with the same mechanism as conventional electrolytes in organic carbonates.<sup>[74]</sup> For example, SEI formed from NaFSA in [C<sub>4</sub>C<sub>1</sub>pyrr][FSA] (where C<sub>4</sub>C<sub>1</sub>pyrr= N-butyl-N-methylpyrrolidinium) was found to be more stable than that from NaFSA in EC/ DEC solvents. These advantages in addition with the wide liquid phase temperature range makes ionic liquid based electrolytes more attractive for NIB applications. Hence, usage of ionic liquid based electrolytes is expected irrespective of their high cost for special applications where the cell operation under harsh environmental condition is required.<sup>[78]</sup> Still, deeper understanding of the electrode-electrolyte interphase chemistry and Na-insertion/de-insertion properties is required before its usage in commercial NIBs. Further, the issues related with high viscosity of ionic liquids, hence high polarizations during Na-insertion/de-insertion need to be solved.

In recent periods, other non-conventional electrolytes, that are much away from the conventional design strategies such as super concentrated organic electrolytes,<sup>[79]</sup> water in salt electrolyte (WISE),<sup>[31]</sup> locally concentrated electrolyte<sup>[80]</sup> etc attracts the scientific community as it exhibits interesting properties such as thermal stability, electrochemical stability etc. However, these electrolyte designs are still in their infancy stage and further analyses need to be carried out to ensure whether these electrolytes could satisfy all the required properties for real-life applications. Currently, the two major drawbacks of these electrolytes being i) their cost because of the need of high concentration (20 M) of Li-based salts and ii) their very high viscosity at low temperature which lead to limited power rate capability.<sup>[81]</sup> Hence, we can hope that further systematic study in these non-conventional electrolytes may help in bringing new dimensions to the NIB field.

Overall, we hope to have conveyed the crucial role of the electrolyte in governing battery performances and the humongous amount of work that is needed to prepare the proper electrolyte configuration with the proper metrics in terms of ionic conductivity, dielectric constant, viscosity

and so on. Optimized electrolytes can contain until 5 or 6 chemicals which because of synergetic positive effects of 2 or 3 additives. In absence of predictive theoretical calculation researchers must rely on field-trial approaches, hence explaining the intense activities in developing high throughput techniques to identify optimized electrolyte formulation. Such an effort together with the development of new *in-situ* techniques to probe interfaces is becoming more important than ever in the past. Future progresses in the development of Metal-ion batteries in terms of durability and reliability will come from progresses at the interfaces rather than at the materials levels. Although tedious research on electrolytes barely provide high impact journals paper, it actually brings the reward of enabling battery technologies.

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Commercial Sodium-ion Battery, SEI, Electrolyte Optimization, Interphase, Electrolyte Additives

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