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Professor Michel Armand is one of the world's leading scientists in the R&D of modern energy storage systems. His scientific works have been devoted to the concepts and technologies of today's batteries, in particular, mastering research on electrodes and electrolytes. With respect to innovative discoveries, Michel had several scientific breakthroughs from the description of the solid-solution electrode and rocking-chair battery to the applications of novel materials utilized in all-solid-state batteries (SSBs); these refer to Li-ion, Na-ion, Li-S, and Li-air cells. At a young age, he formalized the concept of electrochemical intercalation and fabricated the first SSB with sodium-intercalated graphite as the electrode in 1972. Subsequently, he led the use of solid polymer electrolytes and developed lithium-metal-polymer batteries with vanadium oxide as the cathode in 1978. Michel successfully conducted research in new salts topics based on delocalized anions of the sulfonimide family in 1986; his research areas included 1) organic electrode materials, i.e., innovations in redox-active organics, which included poly quinones and aromatic dicarboxylates, and 2) carbon "nano painting" process that has made LiFePO$_4$@C the safest cathode in 2002. Because Michel has co-authored over 500 publications and many patents, it is impractical to fully review his outstanding contributions in electrochemistry in this work. This work is limited to a few of his contributions pertaining to the evolution of electrochemical energy storage. We further discussed different routes envisioned for further progress in rechargeable batteries.

In 1972, Michel Armand attended the NATO conference on *Fast Ion Transport in Solids* in Belgirate (Italy); he presented a new family of interstitial compounds derived from graphite. These compounds are potential tools for solid-state electrode materials. Lithium-ion battery (LIB), formerly known as "rocking-chair" or "shuttle" battery technology, is built on the idea of the flow of Li$^+$ ions back and forth between two intercalation electrodes with different potentials; it was proposed by Armand in the 1970s.[1] On the anode side, the intercalation compound that equips most of the commercial LIBs is graphite. Lithium intercalated graphite (LiC$_6$) was established by Besenhard and Eichinger, who proposed this material as an anode in 1976 in lithium cells. Due to a lack of a suitable electrolyte, the use of graphite as a cathode material at that time was limited. Armand and Duclot solved this problem using polyethylene oxide (PEO)-polymer electrolyte.[2] Armand also established the electrical properties of the PEO-salt complex formed with lithium; he pointed out that this material would be useful as a solid electrolyte for batteries at the Second International Meeting on Solid Electrolytes held in St Andrews in 1978.[3,4] Many works and developments followed; they were aimed at improving the performance and safety of LIBs and lithium metal polymer batteries (LMPBs), Li-S, Li-air and lithium salt for advanced electrolytes, as shown in this review. This list is, however, not exhaustive. Armand further looked into alternative chemistries such as Na-ion batteries,[5–9] mostly at CIC-Energigune (Spain) after 2014. The strategies of this center have been described in a review.[10] This paper first reviews polymers as electrolytes for SSB and devotes the next sections to salts, ionic liquids, and negative electrodes.

Polymers for Lithium Metal Batteries

Lithium-ion batteries, the most widely and currently used electrochemical energy storage systems, have now reached the threshold of their theoretical energy densities (ca. 300 Wh kg^{-1}); however, this is still insufficient to meet the requirements of next-generation batteries ($>$400 Wh kg^{-1}).[11,12] Rechargeable Li metal (Li^0) batteries (LMBs): Li–S and Li–O$_2$ batteries are emerging potential alternatives to LIBs owing to their low electrochemical potential (-3.04 V vs. SHE) and extremely high theoretical specific capacity (3,860 mAh g^{-1}) of the Li^0 electrode.[13] Li^0 is thus believed to be the ultimate choice as a replacement for the state-of-the-art graphite anode material for the next-generation of rechargeable batteries.

Solid-polymer electrolytes (SPEs) offer the perfect solution for the safety concerns and enhance the energy density in a potential safe use.[14,15] They have therefore attracted considerable attention.[16] The commercial use of lithium metal/polymer batteries has been delayed due to 1) the adverse effects of dendrites on the surface of the lithium electrodes and 2) the difficulty in finding a polymer that has both the mechanical strength and ionic conductivity required in a solid electrolyte. Since the first report about ionic conductivity of salts in PEO by Fenton et al. in 1973,[17] PEO has been one of the most widely used polymer matrices owing to its good mechanical properties and the high solvation power provided by either coordination sites.[18,19] PEO-based all-solid-state LMBs operate at elevated temperatures (70–90°C) due to their low ionic conductivity.[20,21] Because of its ability to solvate several salts, its high thermal stability, mechanical properties, compatibility with metal electrodes and reasonable value of ionic conductivity, it is difficult to get rid of PEO.[18,21,22] However, the poor quality of the solid electrolyte interphase (SEI) layers formed between PEO-based SPEs and Li metal electrode leads to an inferior electrochemical performance (e.g., low Coulombic efficiency and short cycle life) of the corresponding all-solid-state LMBs.[23] Therefore, electrochemical properties of PEO-based SPEs had to be improved further with respect to the lithium transference number (approx. 0.2) and electrochemical window (4.5 V). Hence, research has been focused on exploring alternative chemistries for SPEs including polycarbonates, polynitriles, polyalcohols, or polyamines,[24] and salts in recent years.

In particular, carbonate-containing aliphatic polymers have shown excellent electrochemical properties, especially the increased transference numbers. This improvement in electrochemical properties is attributed to the targeted coordination between Li$^+$ and a carbonyl group.[25] Ethylene oxide units have been portrayed as a way to improve the ionic conductivity of polycarbonates whereas a cross-linkable PEO

carbonate polymer precursor has been shown as a potential material to obtain freestanding SPE.[26] However, poor mechanical properties had to be improved. To overcome this drawback, the chemical structure of PEO carbonate was modified by incorporating a methacrylic diol in the polycondensation synthesis.[27] These membranes yielded impressive electrochemical values, such as high lithium ionic conductivity and transference number, $7.4 \cdot \times 10^{-4}$ S cm^{-1} and 0.59, respectively, at 70°C with 30 wt% of LiTFSI.

Aldalur et al. reported a new type of flowable polymer electrolyte (FPE) comprising a variation of a super soft polymer matrix containing polyether side moieties (Jeffamine)[28–30] and sulfonimide salts (i.e., LiTFSI and LiFSI) with the aim of improving the interfacial compatibility with electrode of polymer-based all-solid-state LMBs. When used as a buffer layer between Li-metal anode and PEO-based electrolyte, FPE improves cyclability and Coulombic efficiency of the Li||LiFePO$_4$ cell[31] (Fig. 1). The high amor-
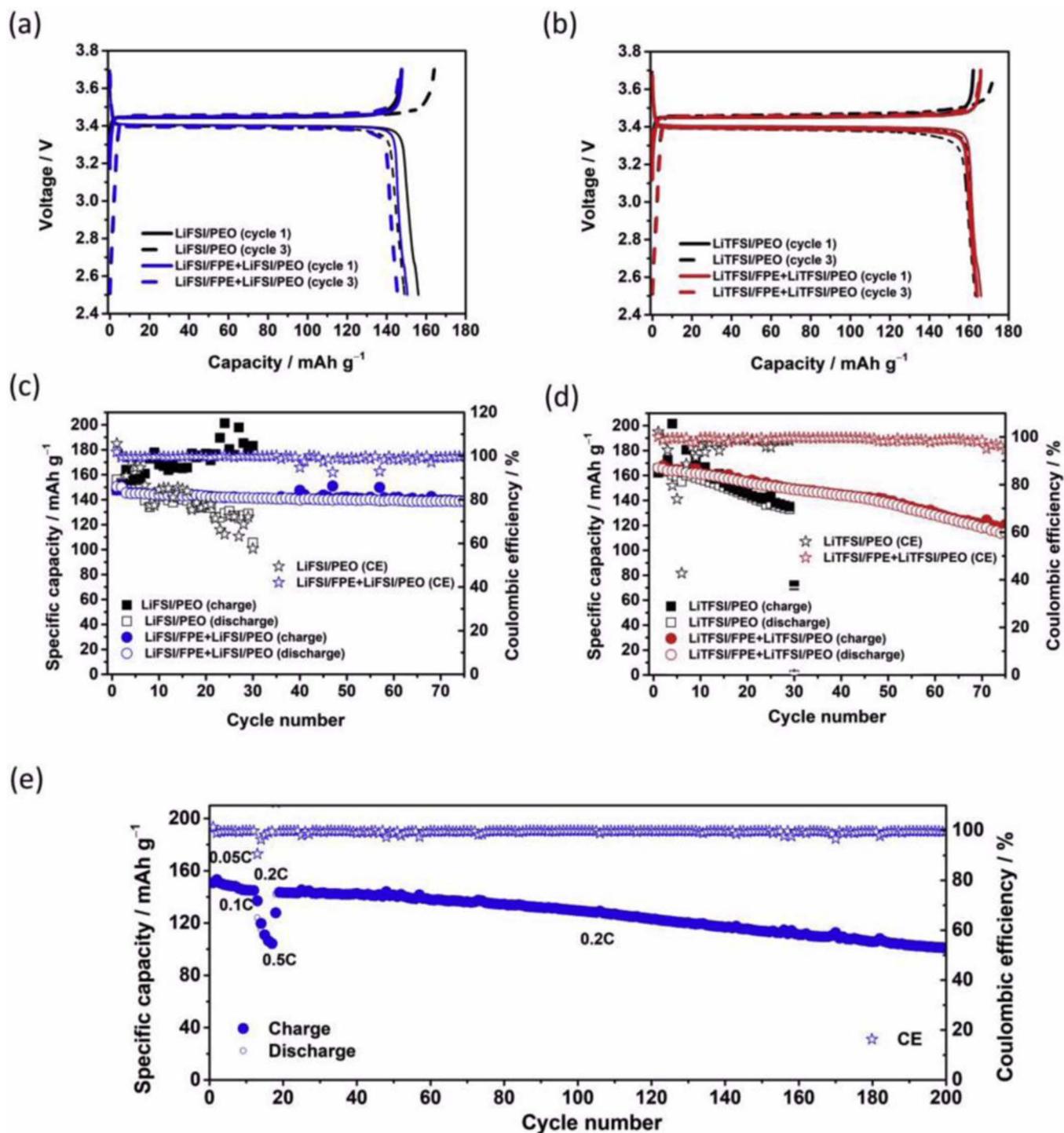
Figure 1. Charge/discharge profiles of the Li^0|SPEs|LFP cells using (a) LiFSI/FPE+LiFSI/PEO and (b) LiTFSI/FPE+LiTFSI/PEO as electrolyte at 70°C under a constant C-rate of 0.1/0.1C. Specific charge/discharge capacities and Coulombic efficiency vs. cycle number for the cells using (c) LiFSI/FPE+LiFSI/PEO and (d) LiTFSI/FPE+LiTFSI/PEO as electrolyte at 70°C under a constant C rate of 0.1/0.1C. In Figure a–d, the results of the reference electrolytes (i.e., LiFSI/PEO and LiTFSI/PEO) are given for comparison. (e) Specific charge/discharge capacities and Coulombic efficiency vs. cycle number for the cell using LiFSI/FPE+LiFSI/PEO as electrolyte at 70°C and different C-rates. Reproduced with permission from Ref. 31

phization and segmental mobility of the liquid-like polymer matrices facilitate fast ionic transport: thus, this leads to the highest ionic conductivity (6.6×10^{-4} S cm^{-1} at 70°C and 1.4×10^{-4} S cm^{-1} at 30°C).

Hierarchical-multifunctional polymer electrolyte (HMPE) was fabricated via in situ copolymerizing lithium 1-[3-(methacryloyloxy) propylsulfonyl]-1-(trifluoromethanesulfonyl)imide (LiMTFSI) and pentaerythritol tetraacrylate (PETEA) monomers in traditional liquid electrolyte, which is absorbed in a poly(3,3-dimethylacrylic acid lithium) (PDAALi)-coated glass fiber membrane.[32] HMPE simultaneously exhibits high ionic conductivity (2.24×10^{-3} S cm^{-1} at 25 °C), near-single ion-conducting behavior (Li-ion transference number of 0.75) at room temperature, good mechanical strength and remarkable suppression for Li dendrite growth. It also effectively suppresses the diffusion of iodine species and therefore enables stable cycling of quasi-solid-state Li-I cells. Furthermore, it can be extended to other alkali metal battery systems based on conversion chemistry, thus opening a new avenue for the development of high-performance energy storage devices.

Block polymerization was also proposed as a strategy to modify the architecture of the polymers at the molecular level;[33,34] the microphase separation properties of block copolymers closely combine the properties of different polymer blocks. For example, redox-active polyimide–PEO block copolymers are used as electrode materials for lithium batteries.[35] An excellent value of discharge capacity of 170 mAh g^{-1} is obtained using the best performing naphthalene polyimide-b-PEO2000 (i.e. having PEO blocks of 2000 g mol^{-1}) that exhibits a good stability after 100 cycles at a current density of 1Li$^+$/5 h with polyimide as the active material. This is attributable to the semi-crystalline structure of this material, which is related to the ability of long PEO segments to crystallize. Furthermore, the example illustrates the attempts to switch from inorganic to organic active materials, which would reduce not only the price but also the carbon fingerprint. However, organic molecules usually dissolve into electrolytes, and this work also shows that polymerization is the best method to fix them.

The addition of both inactive and active inorganic fillers also impacts the cell performance of the polymer electrolytes; they can improve the ionic conductivity and the mechanical strength needed to suppress the dendrites formation at the surface of the lithium electrode. This holds true for any lithium metal battery. In particular, the addition of ceramics nano-powders improves the mechanical properties of PEO-based SPEs as well as their interfacial behavior when in contact with the Li metal electrode.[36] Inert nano-sized Al$_2$O$_3$ fillers in both PEO-LiFSI and PEO-LiTFSI electrolytes improve the cycling stability and capacity retention.[23] With respect to the Li-S chemistry, fillers help capture soluble polysulfides responsible for the so-called shuttle effect that affects the electrochemical performance. For instance, embedding Li-ion conducting glass-ceramic (LICGC) in LiFSI/PEO electrolyte increased the sulfur utilization and areal capacity, but caused poor cycling stability due to the side reaction of LICGC with Li negative electrode. Judez et al. have therefore proposed a bilayer electrolyte configuration where the Al$_2$O$_3$-added membrane faces the Li negative electrode and LICGC-added membrane contact the S cathode. The cell delivered a good areal capacity of 0.53 mAh cm^{-2} with Coulombic efficiency higher than 99% at the end of 50 cycles.[37] The capacity was raised to 0.85 mAh cm^{-2} by 1) adding the nano-sized Al$_2$O$_3$ to the polymer electrolyte as a negative electrode stabilizer and concurrently in the S cathode as PS reservoir and 2) separating Al$_2$O$_3$-added membrane and Al$_2$O$_3$-added S cathode with a filler-free electrolyte membrane.[38] This beneficial effect of the integration of nano-sized Al$_2$O$_3$ to PEO was attributed to the fact that it acts simultaneously as polysulfide reservoir additive in the cathode and as anode stabilizer filler in the electrolyte. This reflects the strategy that entails introducing functional solid additives to polymer electrolytes.[39]

For a filler-free polymer electrolyte, the Li^0 anode surface must be treated for protection and to avoid the growth of dendrites. The growth of dendrites has been considerably retarded in the Bluecar system of Bolloré by the ingenious use of a bi-gyroidal mixture of LiTFSI/PEO and polyvinylidene fluoride (PVDF). This opposes a mechanical bar-

rier to the growth of Li spikes, although only small areal capacities are attainable (1 mAh cm^{-2}).[16,40] Eshetu et al. have recently proposed lithium azide (LiN$_3$) as a novel lithium nitride (Li$_3$N) precursor to form a compact and conductive passivation layer on Li negative electrode;[41] this will lead to an improvement of the electrochemical performance with respect to the results obtained when the precursor of Li$_3$N was 0.1 m azidotrimethylsilane [(CH$_3$)$_3$SiN$_3$].[42] Such protection of the Li^0 anode is of particular interest in Li-S batteries because the lower specific gravity of polymer electrolytes—compared to that of the ceramic-based electrolytes (ca. 1.2 g cm^{-3} for PEO-based electrolytes vs. ca. 5 g cm^{-3} for garnet-type solid electrolytes—make it difficult for ceramics to be used in Li-S batteries. Only the polymer-based all-solid-state Li-S batteries could achieve gravimetric energy densities beyond the capability of the state-of-art Li-ion batteries (>400 Wh kg^{-1}).[14,15]

Lithium Salts

The chemical structure of lithium salts plays a pivotal role in the intrinsic properties of solid polymer electrolytes (SPEs).[22] LiTFSI was suggested as a conducting salt for SPEs by Armand et al. in 1989[43] after seeing an enormous increase in acidity of the remaining proton in the bis(trifluoromethanesulfonyl)imide acid (HTFSI). The high flexibility of the sulfonimide ($-SO_2-N-SO_2-$) group enhances the ionic conductivity by reducing the crystallinity of the PEO matrix owing to the plasticizing effect. The outstanding thermal and electrochemical stability of this LiTFSI, as well as the highly delocalized charge distribution attributable to the dissociation of Li$^+$ due to the flexible S$-$N bond, qualify this salt for the development of reliable SPEs for Li-based batteries.[19] Lithium bis(fluorosulfonyl)imide (Li[N(SO$_2$F)$_2$], LiFSI), an analogue of LiTFSI, has been widely studied due to the improved compatibility with various electrodes such as lithium iron phosphate (LiFePO$_4$, LFP) or lithium cobalt oxide (LiCoO$_2$, LCO) cathodes[44] and Li^0 electrode.[45] This enhanced stability with Li° anode is attributed to the formation of LiF-rich solid electrolyte interphase (SEI) layer, resulting in a stable cycling performance.[19,23] In addition, the substitution of FSI$^-$ for TFSI$^-$ inhibits electrolytic corrosion on an Al current collector[46] at low potential. In the high potential region of 4.0–5.5 V vs. Li$^+$/Li in the binary electrolytes comprising LiTFSI and the TFSI-based ionic liquids, Al corrosion does not occur,[47] although LiTFSI is widely demonstrated to be corrosive in carbonate electrolytes.

A new sulfonimide anion, (difluoromethanesulfonyl) (trifluoromethanesulfonyl)imide (DFTFSI$^-$), was recently proposed as a potential alternative to TFSI$^-$. Although it possesses similar properties as TFSI$^-$, SPEs cationic conductivity is notably enhanced through the hydrogen bond interaction between DFTFSI$^-$ and PEO.[48] Solid polymer electrolytes comprising hydrogen-containing anions demonstrated higher Li-ion conductivities, and they are electrochemically stable for various kinds of solid-state lithium batteries (Li–LiFePO$_4$, Li–S, and Li–O$_2$ batteries).[49] This opens up a new avenue for designing safe and high-performance all-solid-state LMBs in the future.

To increase the transference number—a very important parameter that affects the electrochemical properties—it is essential to fix the anions while leaving the cations mobile. In particular, suppressing the mobility of anionic species in polymer electrolytes is essential for mitigating the concentration gradient and internal cell polarization; this improves the stability and cycle life of rechargeable alkali metal batteries. Different strategies were proposed for immobilizing the anions. One of these strategies is their covalent bonding to polymer/inorganic backbones. This is achieved by, for instance, grafting a negative charge delocalized anion (e.g., CF$_3$SO$_2$N$^{(-)}$SO$_2$—, TFSI-type anion) to a polymer backbone.[40] It is also possible to add anion-trapping molecules into SPEs.[16] For instance, silica (SiO$_2$) yielded a new type of nano-hybrid electrolyte with a high cationic transport number as shown in Fig. 2.[50–52] Unfortunately, these methods sacrifice ionic conductivity significantly. Recently, a new strategy was proposed, using an ether-functionalized anion (EFA) as a counter-charge in a lithium salt.[53] As the salt component in PEs, it achieves low an-
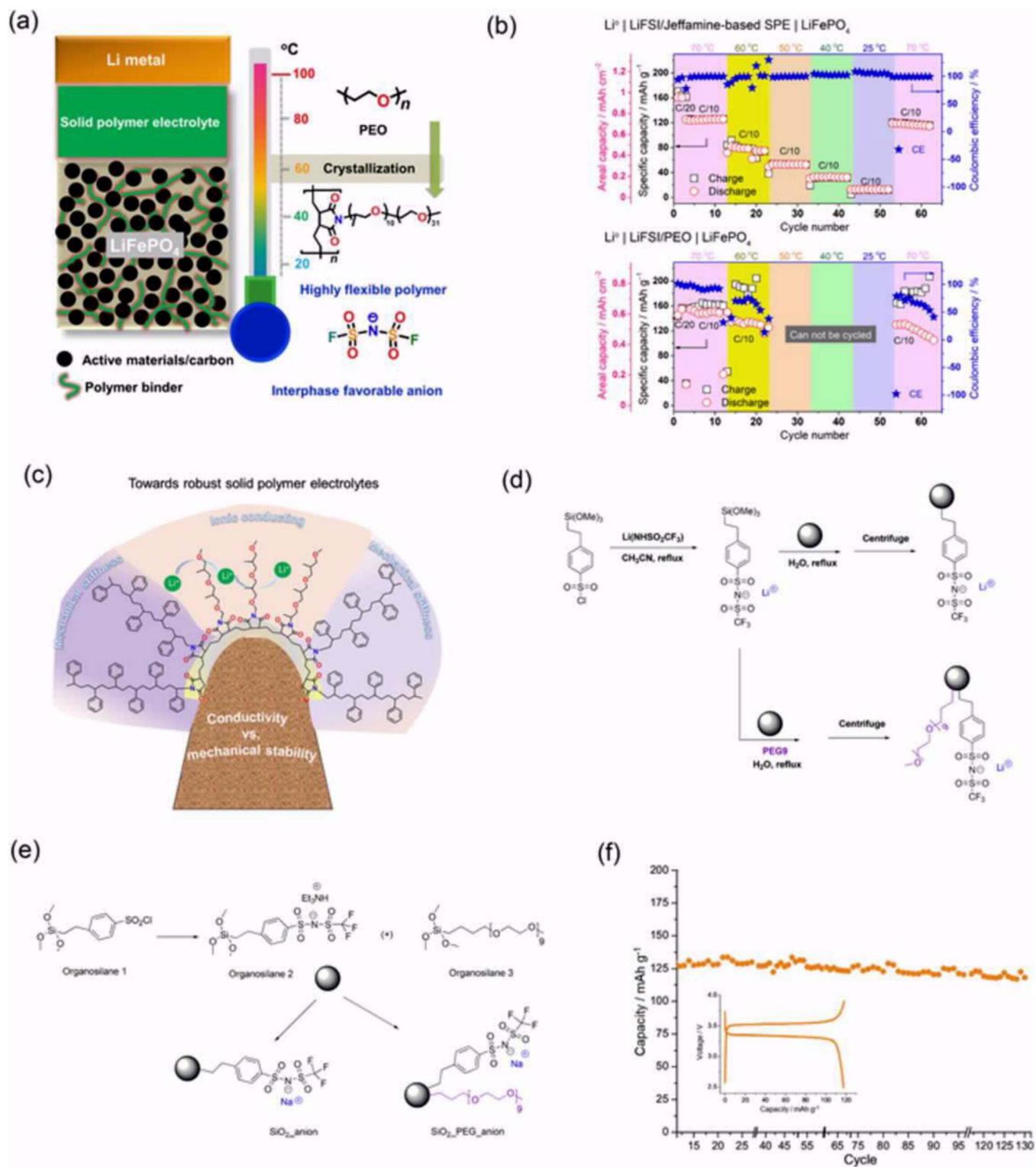
Figure 2. Advanced polymer electrolyte developed in CIC Energigune.[10] (a) Jeffamine-based PEs in combination with SEI-favorable LiFSI salt for RT operation of all-solid-state Li° polymer cells. (b) Cycling performance of the Li⁰‖LiFePO₄ cells using LiFSI/Jeffamine-based (upper) and LiFSI/PEO-based SPEs (down) at various temperatures. Reproduced with permission from Ref. 29. (c) Self-standing highly conductive Jeffamine-based block copolymer electrolytes. Reproduced with permission from Ref. 30. (d, e) Synthetic route for Li-ion (d) and Na-ion (e) conducting nano-hybrid electrolytes. Reproduced with permission from Ref. 52 and Ref. 50, respectively. (f) Galvanostatic cycling of a Li⁰‖LiFePO₄ cell using nano-hybrid electrolytes. Reproduced with permission from Ref. 52.

ionic diffusivity but sufficient Li-ion conductivity. The ethylene oxide unit in EFA endows nanosized self-agglomeration of anions and traps the interactions between the anions and its structurally homologous matrix, poly(ethylene oxide); thus, this suppresses the mobility of neg-

ative charges. In contrast to previous strategies of using anion traps or tethering anions to a polymer/inorganic backbone, this work offers a facile and elegant methodology on accessing selective and efficient Li-ion transport in PEs and related electrolyte materials.

Lithium (fluorosulfonyl)(pentafluoroethylsulfonyl)imide/polyethylene oxide (LiFPFSI/PEO) polymer electrolyte possesses a high ionic conductivity of 6.2×10^{-4} S·cm^{-1} at 80°C. In particular, with the SEI favorable FSO$_2^-$ group in the FPFSI$^-$, the chemical compatibility with Li^0 electrode is significantly improved. These excellent properties qualify LiFPFSI as a potential salt for SPEs-based Li batteries.[54] Another strategy is the use of perfluoropolyether-based liquid polymer electrolytes; they provide a unique "anion-solvent" interaction that effectively inhibits the corrosion of aluminum current collectors, suppresses lithium dendrite growth, and also facilitates the formation of a thin and stable SEI layer on Li anode.[55]

In Li-S batteries, the salts must be chosen by considering the specific problem of the immobilization of the polysulfides. A high salt concentration in the electrolyte helps to impede the polysulphide diffusion rate as a result of "salting out"; Suo et al. have, therefore, systematically studied the effect of LiTFSI salt from 1 to 7 mol L^{-1} in 1,3-dioxolane (DOL): dimethoxyethane (DME) (1:1 by volume) solvent and introduced the concept of "solvent in salt electrolyte" when the Li salt concentration was above 4 mol L^{-1}.[56] High lithium-ion transference number (0.73) was demonstrated, thus resulting in it touted as the most promising electrolytes for Li–S batteries. Such an electrolyte cannot only inhibit the dissolution of lithium polysulfide but also effectively protect a metallic lithium anode against the formation of lithium dendrites. However, these ethers-based electrolytes are still highly flammable and volatile, thus possessing a serious fire hazard. Additionally, it has been shown that DOL can undergo a cleavage, which limits the cycling life of the cells. This was the motivation for the search of different salts-solvents. To stimulate new avenues for the practical realization of the Li-S batteries, various functional additives have been outlined in the existing literature.[39] Ion conductivities of the TFSI-based SPEs still remain low. The substitution of LiTFSI with LiFSI resulted in a significantly improved cycling stability of Li-S cells due to the formation of stable and polysulfide-resistant SEI films in LiFSI-based Pes, which prevented the side reactions of PS intermediates on Li^0 negative electrode.[57] However, FSI$^-$ reacts chemically with PS species via nucleophilic attack on the S—F bond, generating an unstable trivalent anion, which might decompose and irreversibly consume the electroactive materials (i.e., PS species); thus, leading to a lower S utilization. A new salt anion, (fluorosulfonyl)(trifluoromethanesulfonyl)imide anion {[N(SO$_2$F)(SO$_2$CF$_3$)]$^-$, FTFSI$^-$} inherited from the design of lithium salts in polymer electrolytes and the polysulfide species was formed during the cycling. The corresponding Li–S cells deliver high specific/areal capacity (1394 mAh g$_{sulfur}^{-1}$, 1.2 mAh cm^{-2}, in light of the molecular level combination of —SO$_2$CF$_3$ (belongs to TFSI$^-$) and —SO$_2$F (belongs to FSI$^-$)) functionalities.[58] The corresponding Li–S cells deliver high specific/areal capacity (1394 mAh g$_{sulfur}^{-1}$, 1.2 mAh cm^{-2}), good Coulombic efficiency, and superior rate capability (∼800 mAh g$_{sulfur}^{-1}$ after 60 cycles). A fluorine-free noble salt anion, tricyanomethanide [C(CN)$_3^-$, TCM$^-$], was proposed as a Li-ion conducting salt. Compared with the widely used perfluorinated anions, the LiTCM-based electrolytes show decent ionic conductivity, good thermal stability, and sufficient anodic stability suitable for the cell chemistry of solid-state Li-S batteries SSLSBs (high specific discharge capacity of 800 mAh g$_{sulfur}^{-1}$ and high areal capacity of 0.75 mAh cm^{-2} at the first cycle, more stable cycling at high C-rate of 0.2C with high Coulombic efficiency of ≈100%, as well as superior rate capability (≈600 mAh g$_{sulfur}^{-1}$ at 0.5C)).[59] A breakthrough in improving the performance of SSLSBs was obtained recently via a designer anion, (difluoromethanesulfonyl)(trifluoromethanesulfonyl)imide anion (DFTFSI). DFTFSI-based electrolytes show dendrite-free Li^0 plating and stripping, and enable the long-term cycling of Li-S cells with high capacities and excellent Coulombic efficiencies. This study, therefore, opens a new avenue toward the design of new and tailored SPEs for applications in a high-performance and safer Li-S battery as well as other rechargeable Li^0 batteries.[60]

Na-ion batteries represent a low-cost battery system for large-scale energy storage and electric vehicle (EV) applications.[5] To avoid the loss of capacity driving the first cycle due to the formation of the SEI when hard carbon is used as the anode, sacrificial salts such as LiN$_3$ and NaN$_3$ can be used,[61] although they are either toxic or explosive. This was the motivation to consider another salt. A new environmentally benign and cost-effective sodium salt (Na$_2$C$_4$O$_4$) was applied as an additive to the cathode to solve the irreversible-capacity issues of anodes in sodium-ion batteries.[62] A 100% increase in capacity was obtained with this new salt in sodium cells with Na$_3$(VO)$_2$(PO$_4$)$_2$F cathode. Using deionized (DI) water as a solvent for a greener electrode fabrication technique has been observed when using the new sodium salt at a 2C rate. The impact of the salt anions in the electrolyte in Na-batteries has been studied in Ref. 63.

A variety of organic ionic plastic crystals (OIPCs) has been proposed; they constitute a promising class of solid electrolyte. Moreover, they use a variety of cations, including sulfonium,[44] but they have relatively low ionic conductivity, particularly prior to doping.[64] Lithium doping improves conductivity, but the concentration of Li salt doping can be limited to avoid the formation of secondary liquid or solid phases.[65,66] Among the first attempts, LiTFSI:N,N'-diethyl-3-methylpyrazolium bis-(trifluoromethanesulfonyl)imide (DEMPyr123) was proposed with a plastic crystalline phase that extends from 4.2°C to its melting point at 11.3°C.[67] A major improvement has been obtained recently with nano-sized polyvinylidene difluoride (PVdF) particles incorporated with 1:1 (mole ratio) LiFSI:[C$_2$mpyr][FSI], (C$_2$mpyr = N-ethyl-N-methylpyrrolidinium) in a ternary composite.[68] This takes advantage of the fact that the interactions between the –CF$_2$ dipoles on the PVdF polymer chain and [C$_2$mpyr]$^+$ cations in the plastic crystal result in partial amorphization and enhanced ion dynamics of the plastic crystal.[69] The conductivity was raised to 10^{-4} S cm^{-1} at 30°C, and the Li$^+$ transference number was 0.44 ± 0.02 at 50°C; this is the highest value reported so far for a plastic crystal-based electrolyte due to interphase consisting of the OIPC-LiFSI coating the individual, closely packed PVdF particles. Li//LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ cells charged to 4.6 V sustained up to 1,300 charge-discharge cycles at 50°C, highlighting the exceptional stability of these electrolytes (see Fig. 3).

Ionic Liquids

Ionic liquids (ILs) are room-temperature molten salts composed entirely of ions that undergo virtually unlimited structural variations through appropriate modification of the cations and anions.[70] These ionic liquids are also intensively investigated in dye-sensitized solar cells.[71,72] With regard to lithium batteries, the ILs can be used as a reaction medium to synthesize many cathode elements.[73] Among them, the olivine family found an outstanding commercial success, and it will be discussed in the next section. In this section we focus on the use of ILs in electrolytes; they have been studied as a possible and safe alternative to conventional carbonate solvents used in the commercial Li-ion batteries. ILs can reduce risks of thermal runaway and fire accidents.[74]

The attention of ILs as electrolytes mainly focused on Li-battery (i.e., Li metal as anode); this is due to an incompatibility of neat ILs with graphite anode because stable solid electrolyte interphase (SEI) on the surface of graphite required for reversible intercalation of Li$^+$ ions into the graphite cannot be established at first few cycles. Enormous irreversibility is observed in the first cycle.[75] However, many electrolytes based on fluorinated sulfonimide anions containing fluorosulfonyl (FSO$_2$-) group were studied for both Li and Li-ion batteries.[19,45,46,76–78] When ILs molecules are integrated into polymer chains, a new class of materials named Polymeric ionic liquids is obtained. The advantage with respect to PEO-based electrolytes is that the oxidation-prone C–O linkage is avoided, and PILs are more compatible with their archetype ILs. The simple molecular design of PILs offers a peculiar playground for tailoring the properties of PIL-based electrolytes. Owing to their various intrinsic features, such as superior mechanical and chemical stability, structural controllability over the IL species and macromolecular backbone and leak-proof nature and improved safety, PILs are emerging as alternative electrolyte/binder candidates for Li-based rechargeable batteries. A recent
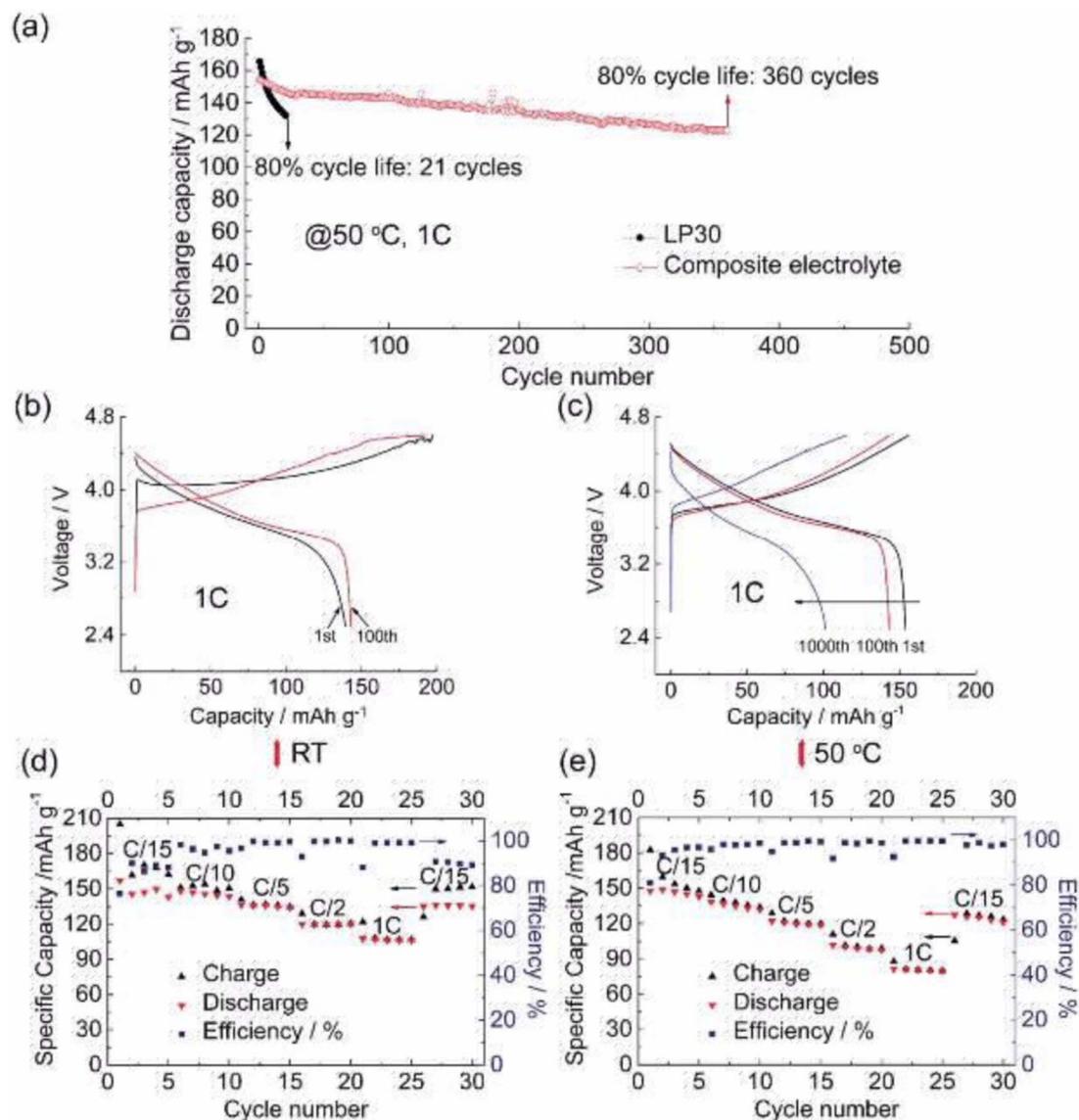
Figure 3. Li‖LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ cell cycling of the 362 nm PVdF-based composite electrolyte consisting in PVdF particles incorporated with 1:1 (mole ratio) LiFSI: [C$_2$mpyr][FSI]. (a) Discharge capacity comparison between LP30 and composite electrolytes for cells cycling at a rate of 1C at 50°C. The endpoints indicate 80% of the initial discharge capacity. Cell cycling at room temperature at 1C: (b) the 1st and 100th charge-discharge curves, (d) charge and discharge capacities of composite electrolyte at different C rates. Cells cycling at 50°C at 1C: (c) the 1st, 100th, and 1000th charge-discharge curves, (e) charge and discharge capacities of composite electrolyte at different C rates. The cutoff voltages for all the cells were from 2.5 to 4.6 V. Reproduced with permission from Ref. 68.

review has been devoted to them.[79] The ion mobility in PILs is affected by many parameters such as the nature of the cation and anion, spacer, molecular weight, and nature of the polymer chain. In 2013, Armand et al. introduced a family of nanohybrid polysalts by functionalizing nanoparticles with delocalized covalent anions while reserving alkali metals as counter cations.[50] The blend of these polysalts with PEO afforded conductive hybrid electrolytes with extremely low anion mobility, thereby leading to a remarkably enhanced cycling performance of Li^0 LFP cells.[52] Imidazolium-based ILs have narrow electrochemical stability windows than other cation-based ILs such as quaternary ammonium, pyrrolidinium, and piperidinium cations[71,78,80] to improve the adhesion of the binder to graphite by chemical bonding upon reduction.

Ionic liquids are also helpful to build ceramic electrolytes. The best example of such a solid electrolyte is LiZnSO$_4$F, a fluorosulfate material of the LiTiOPO$_4$-type structure obtained by using [C$_2$mim][Tf$_2$N].[81] It showed a room temperature ionic conductivity ranging between 10^{-5} and 10^{-7} S cm^{-1} on pressed pellet samples, four orders of magnitude higher than the IL-free LiZnSO$_4$F and an

electrochemical stability window extending from 0 to 5 V vs. Li$^+$/Li. The increment in ionic conductivity of the LiZnSO$_4$F-IL sample could be related to a Li-bearing IL layer grafted onto the surface of the LiZnSO$_4$F particles.

ILs are also applied in the synthesis of electrolytes for Li-S cells. In particular, a novel hybrid electrolyte system composed of *N*-methyl, *N*-propyl pyrrolidinium bisfluorosulfonimide (C$_3$mpyrFSI) ionic liquid and 1,2-dimethoxy ether (DME) at the saturated concentration of LiFSI salt demonstrated the most favorable performance for an IL/DME composition of 80:20 (w:w).[82] Li-DME is likely to form chelation compounds by breaking down the larger ionic aggregates, thus resulting in smaller solvation shell and higher ionic mobility. Due to its ability to suppress polysulfide dissolution and enhance Li transport properties while minimizing the volatile organic solvent component, the hybrid electrolyte system is an excellent candidate to further explore for future Li–S systems (Fig. 4). The choice of C$_3$mpyrFSI over the C$_3$mpyrTFSI in this work was also motivated by the faster transport found in the FSI-based ILs than in TFSI-based ILs. This is attributed to the smaller size of FSI$^-$ anion and lower cation−anion
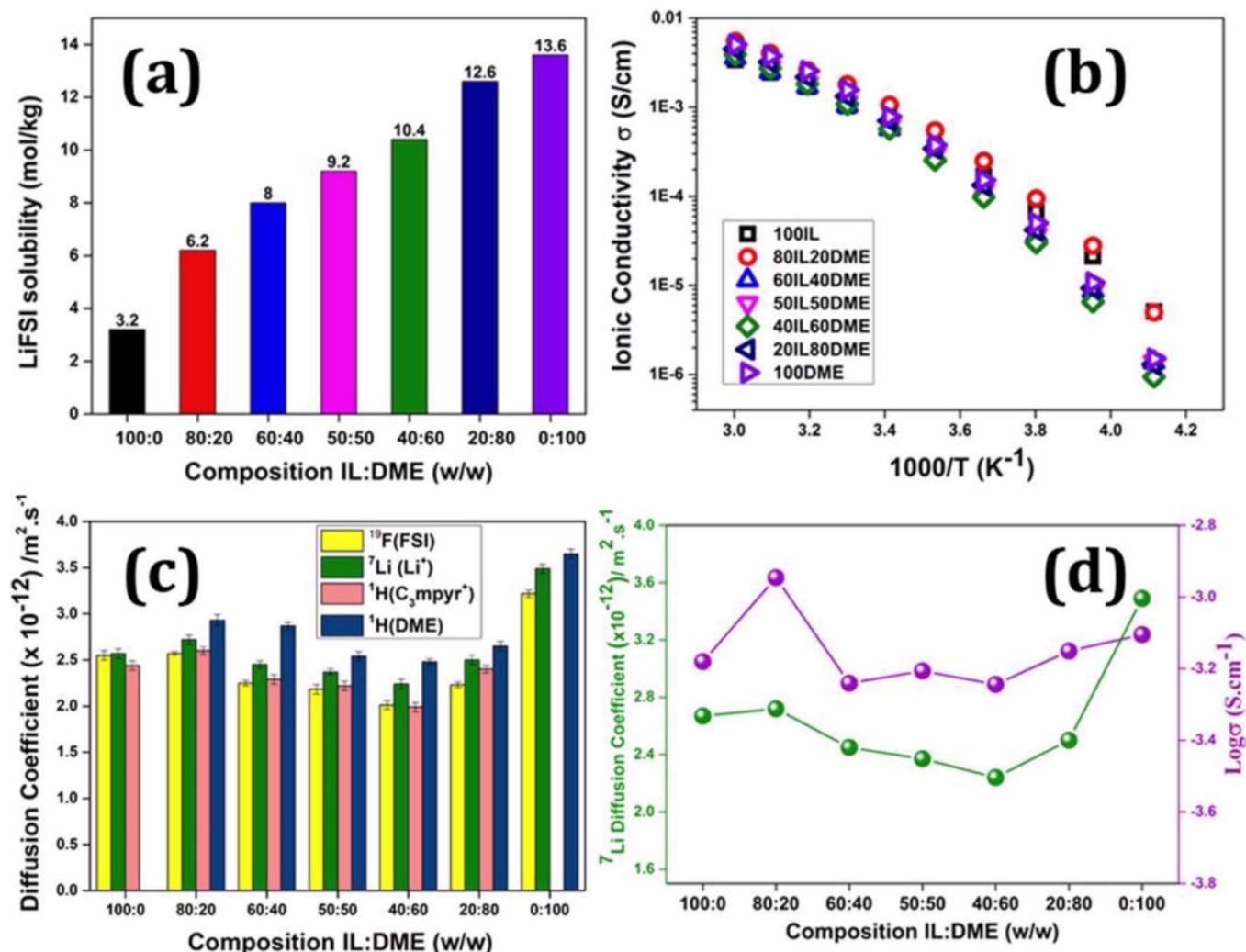
Figure 4. (a) LiFSI salt solubility of various ionic liquid-based hybrid electrolytes based on a mixture of an IL (C_3mpyrFSI) and an ether (DME) in the presence of high LiFSI salt concentration. (b) Temperature-dependent ionic conductivity. (c) Diffusion coefficient values of ionic species of saturated ionic liquid-based hybrid electrolytes. (d) Comparison of ionic conductivity and ^{7}Li diffusion coefficients of saturated ionic liquid-based hybrid electrolytes. Reproduced with permission from Ref. 82.

binding energies.[83] On the other hand, the FSI⁻-based ILs show less thermal stability than the TFSI⁻-based ones regardless of the cation species;[45] this is due to the more liability of FSO_2-function toward pyrolysis.[44] This work was recently shifted to the sodium batteries that hold the promise of a new generation of high energy density and low-cost energy storage technologies. As a result, NaFSI is highly soluble in C_3mpyrFSI allowing the preparation of mixtures that contain very high Na contents greater than 3.2 mol kg⁻¹ (50 mol %) at room temperature. With this IL concentration, the electrolyte can support higher current densities (1 mA cm⁻²) and have a transference number raised to 0.3 to improve the electrochemical performance.[84] The use of ILs is also very promising in Li-O_2 batteries. In particular, an ionic liquid bearing the redox-active 2,2,6,6-tetramethyl-1-piperidinyloxy moiety serves multiple functions as a redox mediator, oxygen shuttle, lithium anode protector, and as the electrolyte solvent. The TEMPO-grafted ionic liquid extended the cycle life of the Li–O_2 battery to 200 cycles with the formation of amorphous Li_2O_2 as discharge products, whereas the overpotential was reduced to 0.9 V.[85]

Positive Electrodes for Li-Ion Batteries

The global LiFePO₄ material and battery market size was estimated at US$ 4.76 billion in 2016, and lithium iron phosphate is projected to grow at the second-highest CAGR of 22.4% by revenue from 2017 to 2025.[86] The use of LiFePO₄ material has helped solve problems of overheating and consequent explosions of batteries. Thus, it was widely used in power generation plants and automobiles. The material was first proposed by Goodenough et al. in 1997. However, several problems had to be solved prior to practical application: (a) LiFePO₄ is a poor electrical conductor, (b) the motion of lithium is a one-dimensional in the olivine framework, and so any impurity will block not only the motion of one Li⁺ ion but also the motion of all the Li⁺ ions in one channel. Furthermore, the ionic conductivity is very sensitive to impurities. Armand played a major role to solve these two problems.

The carbon nano-painting (i.e. coating the LiFePO₄ nanoparticles with a thin layer of conducting carbon) solved the problem of the electrical conductivity.[87] In addition, products from solvent reactions (such as polycarbonates) were not detected at the carbon-treated (C-LiFePO₄) surface when these particles were used as a cathode in the standard electrolyte (1 mol.L⁻¹ LiPF₆ mixture of ethylene carbonate and diethyl carbonate); this is contrary to the findings for other cathode materials.[88] To avoid Fe³⁺ impurities, the synthesis requires well-controlled pH conditions. Although different processes have been found, the eco-synthesis via the use of "latent bases" capable of releasing a nitrogen base upon heating remains the most efficient.[89]

Inspired by the seminal work in 2009,[90–92] considerable attention has recently been paid to the ionothermal method as a novel and

green synthesis route to fabricate cathode materials with engineered properties. Utilizing iron oxalate ($FeC_2O_4 \cdot 2H_2O$) and LiH_2PO_4 as iron-, lithium-, and phosphate-precursors, and $[C_2mim][Tf_2N]$ as a reaction medium, the single-phase $LiFePO_4$ was obtained by heating the suspension at a temperature as low as 250 °C. This prompted extensive studies of other ILs as reaction media for the synthesis of a variety of electroactive cathode materials.[92,93] ILs have a strong impact on the $LiFePO_4$ nucleation/growth rate; they also behave as a structural directing agent. Varieties of ILs were scrutinized with respect to the variation of the anionic components [e.g., BF_4^-, Tf_2N^-, $CF_3SO_3^-$, $C(CN)_3^-$, and Cl^-], cationic centers (pyrrolidinium, imidazolium, and pyridinium), and their carbon chain lengths (C_2–C_8) linked to the imidazolium cations.[73] The IL-induced polarity of the reacting medium and its solvating properties influence the surface energy minimization of the system, thereby affecting the morphology of the particles. In particular, needle-shaped (in the [010] direction) particles of $LiFePO_4$ were obtained by modifying the polarity of the medium and $[C_2mim]^+$ cation with appended polar nitrile groups. On the other hand, platelet-like particles (along the [020] direction) were evidenced in the presence of less polar ILs with longer aliphatic chains (i.e., $[C_{18}mim]^+$ cation). The method was successfully extended to the synthesis of the other olivine compounds.[92,94]

LFP synthesis by the ionothermal route was extended to the synthesis of $LiMnPO_4$ utilizing a variety of ILs as reaction media in the temperature range of 220–250 °C under ambient pressure.[95] Again, the size and shape of $LiMnPO_4$ could be tuned by carefully varying the nature of the IL medium. For instance, the attachment of OH groups to a $[C_2mim][Tf_2N]$ significantly improved the precursor solubility, lowering the reaction temperature from 250 °C to 220 °C and leading to the formation of 200–400 nm $LiMnPO_4$ particles. Conversely, replacing the Tf_2N^- anion with the smaller and more thermally stable triflate anion ($CF_3SO_3^-$) resulted in much easier grain growth, forming slightly larger (300–700 nm) particles. Since then, $LiFeSO_4F$ could also be crystallized from $[C_2mim][Tf_2N]$ in a tavorite phase.[96] This material possesses 3D channels that—in favor of Li^+ ion migration—lead to higher electronic and ionic conductivities and slightly higher voltage compared with $LiFePO_4$.

Other members of the olivine family, Li(Mn, Ni, Co)PO_4 and their mixing have been investigated because their larger redox potential can increase the energy density. Similar to $liFePO_4$, ionothermal synthesis, using pristine ionic liquids (ILs) as reacting media, can be used to produce $LiMnPO_4$ in the temperature range of 220–250°C under ambient pressure.[95] However, this material is even more insulating than $LiFePO_4$, and the carbon coating is more difficult. The trend is now to consider only the partial substitution $LiFe_{1-x}Mn_xPO_4$ as an active cathode element, with $x \leq 0.8$. The replacement of Fe by Co or Ni is even more attractive because it can raise the working potential to 4.8 and 5.1 V, sequentially. The access to the Ni^{3+}/Ni^{2+} couple at 5.1 V versus Li^+/Li is plagued by the formation of intrinsic lattice defects as well as by the oxidation of available electrolytes. On the other hand, access to the Co^{3+}/Co^{2+} couple of $LiCoPO_4$ at 4.8 V vs. Li^+/Li is more promising. In a recent review of these olivine compounds, we have given reasons to be optimistic about the future of $LiCoPO_4$ as a combination of surface modification. Doping now makes it possible to achieve a stable capacity of 140 mAh g^{-1} over 250 cycles.[97] These results justify more research on the SEI and a concomitant study of different electrolytes and separators working at this voltage of 4.8 V.

Until recently, the electrochemical window of conducting polymers did not exceed 4 V, thus limiting their use in solid-state batteries equipped with cathode elements that did not exceed this redox potential vs. Li^+/Li (in practice, $LiFePO_4$, and $Li_{1.2}V_3O_8$). Lithium metal-polymer solid-state batteries with nano C-$LiFePO_4$ and nano $Li_{1.2}V_3O_8$ counter-electrodes (average particle size 200 nm) were studied by in situ SEM and impedance during cycling.[98] This study shows that the cycling life of the nano $Li_{1.2}V_3O_8$ is limited by the dissolution of the vanadium in the electrolyte, which explains the choice of nano C-$LiFePO_4$ (1300 cycles at 100% DOD). With this olivine, no dissolution

is observed. This is the reason for the success of the "Bluecar" commercialized by Bolloreánd equipped with a $LiFePO_4/SPE/Li$-metal battery.

Cathodes for Li-S Cells

The Li-S battery is known to be one of the most promising electrochemical technologies for "post-lithium-ion" batteries, owing to its higher specific energy (2500 Wh kg^{-1}, 3 to 5 times higher), along with its economic and environmental benefits. However, difficulties with the Li-S chemistry with respect to the former LIBs come from the S-cathode. We have already mentioned these difficulties including the shuttle effect due to the soluble polysulfides. Many attempts and progress to understand and avoid these problems have been made since the seminal work of the Nazar's group in 2010.[99] M. Armand started R&D on Li-S batteries with Hydro-Québec in 1982.[100] Among the strategies to suppress the shuttle effect in Li-S batteries, a mechanofusion technique was applied for the first time to confine the sulfur particles inside a stable outer layer of carbon-coated $LiFePO_4$.[101] The S-LFP cathode showed an initial capacity of 1200 mAh g^{-1} at 0.1 C and 80% capacity retention after 90 cycles at 0.5 C. Specific energy of 417 Wh kg^{-1} and energy density of 623 Wh L^{-1} are achievable with this novel technology. The results suggest that the LFP layer enhances the utilization of active sulfur and lowers the polarization for the oxidation of Li_2S_2/Li_2S. This process is appropriate to scale-up without adding much process cost. Recently, studies have proposed the modification of active material (e.g., organosulfur).[102] Another problem comes from the fact that S is insulating. In practice, the problem is overcome by the addition of a large amount of conductive carbon to the sulfur in the cathode; however, ts reduces the energy density of the Li-S batteries. Another strategy is the addition of a redox mediator. The aim of using redox mediators is to improve the utilization of active materials and kinetics of the systems. They experience an oxidation/reduction process at the electrode surface and diffuse later to the active material. Moreover, they oxidize/reduce the active material and diffuse again back to the electrode surface, thus closing the cyclic process. Most of the redox mediators in Li-S systems enhance the utilization of the Li_2S active material in cathodes by enabling its activation at lower potentials. Another type of redox mediator was introduced by Hernández et al.[103] As a binder of the S electrode, they used a polymer with mixed conductivity (ionic and electronic), whose redox process (a polyimide) was within the operating voltage of the Li_2S_n species. This allowed the carbon content of the cathode to be markedly decreased to about 5 wt%.

Concluding Remarks

Michel Armand played an important role in the research and development of all the elements of both lithium and lithium-ion batteries. Today, most of the commercialized batteries for applications that require high-energy-density are Li-ion batteries equipped with liquid electrolytes. The "Bluecar of the Bolloré group" remains an exception. The formation of dendrites on the lithium anode, in particular at high C-rates, in addition to the difficulty of finding polymers that are conductive and stable above 4 V are the main reasons that hindered the development of the all-solid-state lithium batteries. The works on $LiFePO_4$ were determinant to the development of Li-ion batteries because this material improved the safety of the lithium-ion batteries significantly. However, this cathode works at a potential of 3.5 V, and the race after higher energy densities was the motivation to develop other cathodes of the 4 V class, in particular, NCA (Ni-Co-Mn oxides doped with Al). The corresponding Li-ion batteries have an increase in energy density. The drawback is a safety issue because the equilibrium partial pressure of oxygen in transition metal oxides varies exponentially with the voltage. This is done so that the cathodes can have an increase in propensity to lose their oxygen, which results in thermal runaway. Because the organic liquid electrolytes are flammable, the result is a battery fire, and the safety of the electric vehicles equipped with such batteries relies on the battery monitoring

system. The race for the increase in energy density will motivate the research on other cathode elements. Among olivine materials, LiCoPO₄ is impressive for this purpose considering that the strong bonding between P and O in the PO₄ unit should help in the safety of the material, which should avoid the problem of loss of oxygen in transition metal oxides.[97]

The shift from fossil fuel energies to green energies strongly motivates the development of lithium-ion and lithium metal batteries. However, these batteries are "green" only after being manufactured. In particular, the extraction of the transition metals entering the composition of the cathode is not only expensive but also has an immense carbon footprint. His carbon footprint is rarely discussed in the papers but is considerable in the science community. Many efforts in research are therefore focused on organic electrodes. A recent review points to the recent progress in this field, especially to solve the problems of the dissolution of the organic molecules in the electrolyte.[104] As mentioned, the problem of dissolution has been solved by polymerization or grafting. The low operating voltage of the organic electrodes will preclude their use for high power applications such as electric vehicles. However, the very long cycling lives and the fast kinetics reached recently make them competitive with inorganic electrodes for other applications and suggest their use in grid storage and regulation for instance.

Since the pioneering work of Armand et al. on the use of polymer electrolytes for lithium batteries, major efforts have been made to overcome the drawbacks mentioned earlier in this review—concerning the electrochemical window and the conductivity—so that there is a regain of activity on the all-solid-state lithium batteries. The incorporation of ionic liquids in polymer electrolytes improved the conductivity significantly. Parallel to the progress on the electrolyte, the development of lithium salts such as LiFSI and LITFSI in combination with amorphous polymer hosts yielded better conductivities.[105] One major advantage of Li metal batteries is safety. The solid polymer electrolyte prevents the flammability of the liquid organic electrolytes. In addition, with no liquid solvent, its vapor pressure is low, and it is less prone to react with lithium at its melting temperature. Another advantage is the lower price. The current collector for Li-ion batteries is usually copper on the negative electrode, which is expensive; the lithium metal, on the other hand, acts simultaneously as the active element and the current collector. Another issue is the lower cost of the fabrication of the lithium metal polymer battery. The Li metal-polymer cell is low cost through high-speed processing to produce commercial LPCs that contain about 2.5 km of film per battery. It also prevents the formation of the solid-electrolyte interface that must be controlled by the initial formation procedure of Li-ion batteries, which is time-consuming and decreases productivity. Among other chemistries envisioned for the next generation, we have mentioned Armand et al. recent works. They demonstrate that it is now possible to obtain Li-S batteries with very good utilization of sulfur with a cathode that contains only 5 wt% carbon. This improves the volumetric energy density significantly and long cycle life. Li-S batteries are already commercialized.

The challenges and issues facing lithium metal for solid-state rechargeable batteries have been reviewed.[106] The advances in research in the last years[24] suggest that the next generation of rechargeable batteries could be all-solid-state lithium batteries. This includes the case of Li-air batteries that can now reach long cycling life with the advantage that all-solid-state batteries enable the fabrication of flexible batteries because leaking is inevitable with liquid or even gel electrolytes. Among these aforementioned different options for the next generations of rechargeable batteries, it is difficult to predict which one will be the winner. Nevertheless, they all have in common the important contribution of Michel Armand to pave the way to their optimization.

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