Perspective

Fluorinating Interphases

Chunsheng Wang,[1,*,z] **Ying Shirley Meng,**[2,**,z] **and Kang Xu** [3,*,z]

[1]*Department of Chemical and Biomolecular Engineering, University of Maryland College Park, College Park, Maryland 20742, USA*
[2]*Department of NanoEngineering, Materials Science and Engineering, University of California San Diego, La Jolla, California 92093, USA*
[3]*Electrochemistry Branch, Sensors and Electron Devices Directorate, U.S. Army Research Laboratory, Adelphi, Maryland 20783, USA*

Electrode/electrolyte interphase in Li-ion batteries is a critical component that ensures reversible cell reactions far from thermodynamic equilibria. The desired chemical composition and morphology for such interphase, however, remain controversial. Recent advances in battery chemistries and their electrolytes demonstrated that the presence of fluorine in the interphase, either in the form of simple inorganic fluorides (LiF) or organofluoro-moieties, brought positive impacts on the electrochemical performances. Beside the identification of chemical composition, understanding how these fluorinated species exists and distribute in the interphase might constitute the key know-how for the next generation battery chemistries. This is a topic that the battery research community should focus their attention on.

In electrochemical devices of reversible energy storage (e.g., rechargeable batteries, double-layer capacitors), electrodes therein were often designed to operate at potentials far beyond the stability limits of electrolytes. The reversibility of such devices is thus ensured by the kinetic stabilization of electrode/electrolyte interfaces, which involves the sacrificial decomposition of either electrode or electrolyte materials, or both.[1,2] These decomposition reactions result in an independent phase of new materials at the interface (hence called *interphase*), which exists in nanometric scale, remains conductive to the ions of significance to the cell reactions but insulates electron tunneling between electrode and electrolytes.[3,4] The most prominent interphases are certainly those in Li-metal or Li-ion batteries (LIBs), first named "solid-electrolyte-interphase (SEI)" by Peled for such passivation layers on Li-metal,[5] then transplanted by Dahn et al. for similar passivation phenomenon on graphitic anodes surfaces,[6] and more recently adapted for cathode surfaces by Winter et al. as "cathode-electrolyte-interphase (CEI)".[7] Interphases in LIBs often dictate the cycle-life, power density, round-trip energy efficiency, and energy density.

Current Status

Although the successful commercialization of LIB has prompted intensive research on interphases, after investigations of nearly four-decades, interphases is still the most elusive and the least understood components in batteries,[8] not only because of their nanometric existence, in-situ manner of formation but also their extreme sensitivity toward ambient conditions and characterization tools. The chemistry, morphology and formation mechanism of interphases were often found to be entangled with both electrolyte composition as well as surface chemistries of active electrode materials, making the comprehensive understanding rather challenging, even with the aid of diverse in-situ/operando probes and powerful computational simulations.

One peculiar issue of interphasial chemistry is the role of fluorinated species. Early efforts recognized the solvent decomposition as the main chemical source for SEI on anode, which includes semi-carbonates, alkoxides, oxalates and polymeric species.[3,4] Flu-

orinated species such as LiF or fluorophosphates (PO_xF_y), although found universally throughout SEI, were often considered as hydrolysis by-products from the labile fluorinated salt anions (PF_6^-, BF_6^-, or AsF_6^-). As inevitable consequences of these anions that are highly sensitive to trace moisture, the fluoride species in interphases were generally regarded as harmful to the functions of interphases. This belief is supported by the knowledge that LiF in its bulk state is an excellent insulator to both ionic and electronic transport.

More recent works on new battery chemistries, both anode and cathode, start to reverse the above negative impression about fluorides. In most cases, electrolyte systems that could effectively support these aggressive chemistries contain rich sources of fluorine, either in the form of salt anions at high concentrations, or in the form of solvent molecules that bear fluorine-substituents. This "fluorine benefit" could be exemplified by the following representative scenarios:

(1) For silicon-based anode materials,[9,10] whose 300+% volume change presents much more severe challenge to the cell reversibility than graphite anode materials, fluorinated ethylene carbonate (FEC) has become an indispensable co-solvent;

(2) For Li-metal anode,[11] which not only experiences volume change but also presents the most reactive surfaces toward electrolyte, both electrolytes with unusually high salt concentration and highly fluorinated solvents proved effective in stabilizing the Li-metal reversibility. The former is represented by 4.0 M lithium bis(fluorosulfonyl)imide (LiFSI) in dimethyl ether (DME), in which the highest coulombic efficiency (CE >99.5%) of Li-metal was achieved,[12] and the latter by an "*all-fluorinated*" composition that yields the highest CE (99.2%) for carbonate solvents that has been considered intrinsically unstable against reduction by Li-metal;[13]

(3) For high voltage cathode materials such as 4.6 V $LiNi_{0.5}Mn_{1.5}O_2$ or 4.8 V $LiCoPO_4$, either highly fluorinated electrolyte composition[14] or fluorinated electrolyte additives[15] were required to stabilize the highly reactive cathode surface at charged state;

(4) For the well-established graphitic anode materials, extra fluorine-source, usually in the form of high salt concentrations, could enable electrolytes based on "*unconventional*" solvents to support reversible lithiation of graphite with the formation of stable and protective SEI, which would be impossible otherwise. Examples of these "*super-concentrated electrolytes*" include

*Electrochemical Society Member.
**Electrochemical Society Fellow.
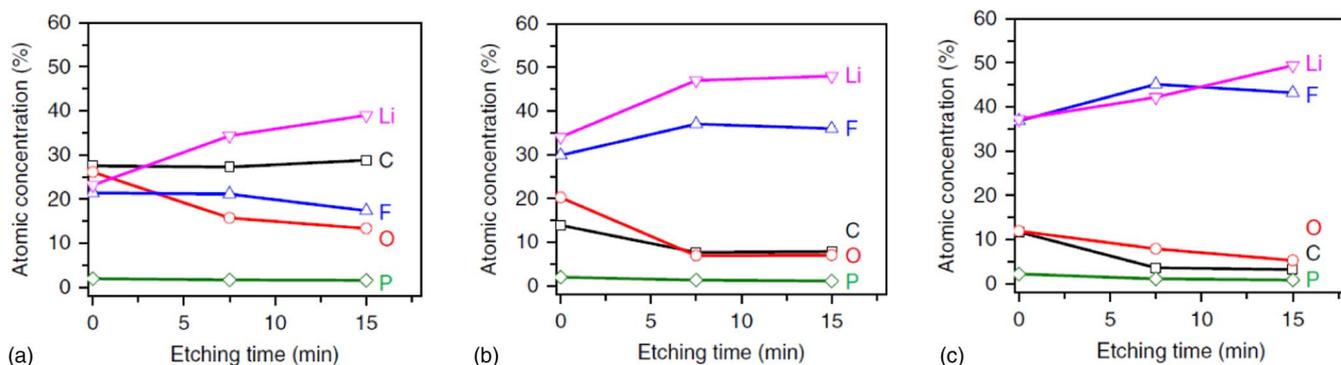zE-mail: cswang@umd.edu; shmeng@ucsd.edu; conrad.k.xu.civ@mail.mil

Figure 1. The fluorine content in the SEIs on Li-metal surfaces as formed from (a) baseline electrolyte (1.0 M LiPF$_6$ in ethylene carbonate/dimethyl carbonate 50:50); (b) moderately-fluorinated electrolyte (1.0 M LiPF$_6$ in fluoroethylene carbonate/dimethyl carbonate 50:50); and (c) all-fluorinated electrolyte (1.0 M LiPF$_6$ in fluoroethylene carbonate/2,2,2-trifluoroethylmethyl carbonate/1,1,2,2-tetrafluoroethyl-2',2', 2'-trifluoroethyl ether 20:20:60). The atomic concentration of each element were derived from X-ray photoelectron spectra under different duration of Ar-sputtering. Note that the composition of SEI formed from (c) converges to a high fluorination degree with LiF as the majority. Reproduced with permission from Ref. 13. Copyright of *Nature Nanotechnology* 2018.

propylene carbonate (PC),[16,17] ethers,[18] nitriles,[19] sulfones,[20,21] and, in the most extreme case, water.[22–26] These alternative chemical source for interphase chemistry significantly relaxed the constraints imposed by the limited choices of solvent species, and expanded the menu for electrolyte formulation.

Analyses on the SEIs and CEIs formed in these electrolytes invariably reveal high content of fluorine species, in the form of either LiF or C-F[13–15,22–26,27] (Figures 1a–1c), which seemed to be responsible for the rather dense and homogenous passivation film morphologies (Figures 2a and 2b).

The most pronounced examples were perhaps the SEIs formed from aqueous Li or Na electrolytes based on high concentration of

bis(trifluoromethane sulfonyl)imde (TFSI) salts (21 m for Li and 9 m for Na, Figures 2c and 2d),[22,26] where the main interphases seemed to be constructed with almost perfectly crystalline LiF as visualized under transmission electron microscopes. This observation, in combination with the fact that the corresponding Li- or Na-ion cells can actually operate at decent or even high rates, cast doubt on the long-standing conviction that fluorides are harmful to the basic function of interphase, i.e., allowing transport of ions. Somehow, via a mechanism that is yet to understand, the transport of ions is not hindered through those SEIs of almost perfectly crystalline LiF- or NaF. This paradox might be better understood in the light of the work by Zhang et al., who demonstrated with both computation and experiment that the interfacial contacts between LiF and Li$_2$CO$_3$, which is another fre-
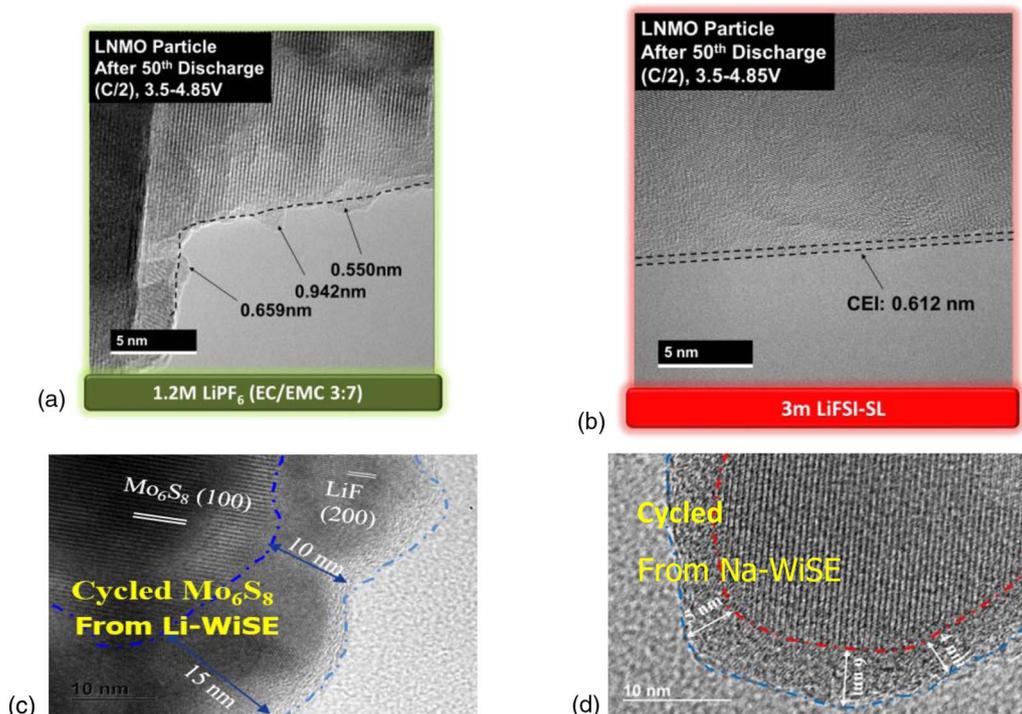

Figure 2. Interphases under transmission electron microscope: The CEI thicknesses on high voltage cathode material LiNi$_{0.5}$Mn$_{1.5}$O$_2$ (LMNO) recovered after 50 cycles from (a) baseline electrolyte (1.0 M LiPF$_6$ in ethylene carbonate/dimethyl carbonate 30:70); (b) super-concentrated electrolyte (3.0 M lithium bis(fluorosulfonyl)imide in sulfolane, Reproduced with permission from Ref. 21. Copyright of *Materials Today* 2018); and the nearly perfect metal fluoride SEIs formed in Li or Na "water-in-salt" electrolytes: (c) Mo$_6$S$_8$ recovered from 21m lithium bis(trifluoromethane sulfonayl) imide in water (Reproduced with permission from Ref. 22. Copyright of *Science* 2015). (d) NaTi$_2$(PO$_4$)$_3$ recovered from 9 m sodium bis(trifluoromethane sulfonayl) imide in water (Reproduced with permission from Ref. 26. Copyright of *Adv. Energy Mater.* 2017).

quent interphasial component and a close structural similarity of semi-carbonate, promotes space charge accumulation along their boundaries, hence generating a pathway of high ionic conduction.[28] Indeed, even in those interphases formed from the only chemical source (TFSI) in aqueous electrolytes, the seemingly pure LiF or NaF layers still contain "impurities" such as Li_2O and Li_2CO_3 [29], whose presence is sufficient to create such ionic pathways.

Future Needs and Prospects

It is beyond doubt now that the presence of fluorinated interphases brought tangible benefits: expanded electrochemical stability window, higher inertness toward both chemical corrosion and mechanical disruptions, and even high ionic transport. The new consensus that gradually takes shape in the community is no longer whether interphases should be fluorinated, but how. For example, fluorine existing in the HF form is known to inflict harm on the interphase and eventually the electrochemical performances of the device, while converting HF into a more useful fluorine form brings benefits.[30] As both Xu and Lucht pointed out separately, the morphology and arrangement of diverse chemical components in interphases might be as important as the chemical composition themselves.[4,31,32]

In the absence of fundamental understanding of how the fluorinated species exists (valence, morphology, distribution and interaction with other interphasial species) in those interphases, the fluorinating attempts so far remain semi-empirical with limited help from computation simulation and spectroscopic characterizations. For example, the use of an all-fluorinated electrolyte formulation ensures all components in that formulation (solvent molecules and salt anion) have the opportunity to serve as fluorine-delivery vehicle during the interphase-formation stage, but such a drastic measure might be an "over-kill". Knowing exactly which component functions as the key fluorinating agent for the upcoming interphase constitutes the key knowledge to enable future battery chemistries,[33] which requires close collaboration among scientists with diverse expertise in modeling, advanced characterization and chemistry/electrochemistry of materials. In particular, understanding precisely how these electrolyte components assemble and arrange, before the interphase formation, in the inner-Helmholtz region near either anode or cathode surfaces might serve as a very useful tool in predicting which component is the key delivery vehicle for fluorine.[34,35]

Conclusions

As the element most resistive toward both oxidation and reduction, fluorine seems to be a desired ingredient for new interphases designed to support aggressive battery chemistries. However, caution should be exercised, as how fluorine exists and distributes in these new interphases matter more than how much fluorine can be introduced. We believe that the knowledge about how fluorine should exist in interphase constitutes a key know-how for designing new electrolyte systems for aggressive battery chemistries of the future, hence more resources should be directed this way.

Acknowledgments

ORCID

Kang Xu https://orcid.org/0000-0002-6946-8635

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