Manipulating interphases in batteries

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Charge-transfer across electrolyte/electrode interfaces dictates kinetics and reversibility of cell reactions within electrochemical devices. When the device operates beyond the thermodynamic stability limits of electrolytes, ‘interphases’ form at the interfaces [1,2]. In the pursuit of new battery chemistries that promise ambitious energy densities, electrolytes often take the blame for failing to support the cell reactions, while in most cases the real culprit is the interphase instead of the bulk electrolyte components themselves. Being able to manipulate the chemistry and morphology of such an important sub-component holds the key to the success of these new battery chemistries.

Electrolytes and interphases are independent but intimately related entities, with the former serving as the chemical parent to the latter. The importance of interphase is best highlighted by lithium-ion batteries (LIB), whose intercalation-chemistry is made possible only with the formation of interphases during the cell activation. Although not fully recognized in pre-LIB era, interphases are prevalent in nearly all batteries operating above 3.0 V, with the venerable Li/thionyl chloride primary battery as an example [3]. It was the success of LIB that brought the science of interphases under the spotlight. The fundamental understanding achieved in the past two decades has allowed us to effectively manipulate the chemistry and properties of interphases, hence decoupling them further from bulk properties. The most extreme example is perhaps represented by the ‘Water-in-Salt’ electrolyte, where the electrochemical stability window of water was expanded to >3.0 V thanks to a designed interphase based on LiF, far beyond what Pourbaix limits (1.23 V) define for hydrogen and oxygen evolutions [4,5]. This successful separation of interphases from their aqueous parental electrolyte opens an avenue to the ‘uncharted water’ of high-voltage aqueous electrochemistries [6], inspiring more aggressive manipulation of interphases for new battery chemistries.

It is generally accepted now that an interphase must insulate electrons while conducting ions that are of significance to the cell reactions (such as Li$^+$ for LIB). It was this electrolyte nature that earned it the popular name ‘SEI’ (solid electrolyte interphase) [7]. Due to significant departure of their potentials from the thermodynamic limits of electrolytes, anode surfaces in LIB induce most of the interphasic chemistry [2]. Chemical analyses on these interphases have identified the electrolyte solvents as the major chemical contributors to interphases, while the salt anion participation remains elusive. This remains true in part because of the ‘diluted’ electrolyte solutions (∼1.0 M) used in the state-of-the-art LIB, in which the Li$^+$-solvation-sheath is sufficiently populated with solvent molecules. According to the formation mechanism proposed by Xu et al. [8–10], such a primary solvation-sheath serves as the chemical precursor of SEI via a transient ternary intercalation compound stage, so reduction of solvent molecules (mostly carbonate esters) dominates the surface chemistry (Fig. 1, left).

This ‘solvent-signature’ on SEI will be reduced or even eliminated when the salt is used at unusually...
high concentrations (>5 M). In such ‘super-concentrated electrolytes’ that are currently explored as solutions to most of the electrolyte-related challenges, the population of solvent molecules are so sparse that a cation simply cannot recruit sufficient molecules into its primary solvation-sheath as it does in diluted electrolytes. Consequently, the anions are forced into the solvation-sheath to answer the calls from electroneutrality and solvation thermodynamics, and their presence therein significantly increases their participation in interphasial chemistry, leading to numerous unexpected chemical as well as electrochemical scenarios due to the unique anion-originated SEIs [4–6,11,12]. At least in the case of ‘Water-in-Salt’ electrolytes (where lithium salt was used at an astonishing concentration of 21 M), density function theory calculations revealed that the high probability of anion in cation solvation-sheath might not be the only reason for a different interphasial chemistry, because the reduction potential of anions in super-concentrated electrolytes also shifted accordingly to a higher level, making it possible for the anion reduction to occur before water molecules do (Fig. 1, right) [4]. Compared with traditional approaches through additives, such alteration of cation solvation-sheath structure provides a more direct manner for manipulating interphasial chemistries.

Despite the decade-long investigations on SEI, many questions still await answers. The most puzzling question is perhaps how Li$^+$ conducts through SEI. Recent experimental and computational results seemed to describe the interphase as an ion-exchange matrix, where the ‘immobilized’ Li$^+$ is sequentially displaced by Li$^+$ moving from either bulk electrolyte or electrode under electric field [13,14]. Yet, this picture is challenged by the discoveries that crystalline LiF, which is essentially an insulator to both electron and Li$^+$, can serve as SEI in ‘Water-in-Salt’ electrolyte while supporting high rates of cell reactions [3] and that transition metal (Mn, Ni, etc.) deposition on anode even at ppm-levels, which should be far below that required to completely block the above Li$^+$-conduction pathway across the interphase, can completely ‘poison’ the SEI [15,16]. An unambiguous resolution of these issues is expected to provide us with more powerful tools to design and manipulate interphases in batteries.

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Special Topic: Energy Storage Materials
Flexible batteries ahead
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While there has been much recent research on the development of flexible or wearable electronic devices that can be integrated into clothes, glasses, watches and even skin, a bottleneck in this technology appears to be the power source. Thus, one of the most significant issues impeding the success of these newly developed portable gadgets is the development of flexible electrochemical energy-storage devices, which can convert chemical energy and electricity, reversibly. Currently, the most suitable candidates for this purpose are flexible batteries, in particular, lithium-ion batteries (LIBs). Flexible batteries are devices that can work in a range of elastic states and retain electrochemical performance during various deformation processes, such as stretching and bending [1].

Until now, the flexible batteries for which there are the most reports are bendable LIBs. Similarly to the key