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Editorial

Weakly solvated electrolytes conducive to uniform lithium deposition

Rechargeable lithium metal batteries (LMBs) meet the demands of high-energy applications in electric vehicles and truck transportation [1–4]. Yet, the low coulombic efficiency (CE) hinders the widespread application of Li anode, which is closely related to the electrolytes [5–7]. The CE of traditional electrolytes for Li anodes is closely related to the speciation of the plated Li during cycling, where fluorinated solvents with weakly solvated Li^+ usually exhibit larger Li deposition particles with higher CE [8,9]. But the relationship between the morphological difference and CE in different electrolytes is less studied [10,11]. There are three relationships between the deposition kinetics of interface Li and the cycling of the battery, no correlation, positive correlation [12,13], and negative correlation [14,15] have been reported on active Li anodes, which neglects the reactivity of Li metal in kinetics. Solid electrolyte interphase (SEI) was formed by the electrolytes reacting with Li, and Li deposition can occur on the Li/SEI interface or the fresh Li/electrolyte interface [16,17]. Each pathway has different deposition kinetics. Therefore, in order to understand the relationship between electrolyte kinetics and lithium deposition morphology, it is important to solve the kinetics of the two ways in the electrolyte.

Based on this, Cui's group proposed that the thermodynamics of the solvation strength of Li^+ in different electrolytes affects the Li deposition morphology [18]. To verify this view, Li^+ solvation behavior, Li nucleation behavior, and plating mechanism in different electrolytes were studied. Firstly, two kinds of deposition pathways with kinetic parameters need to be considered to link interfacial dynamics and cyclability. When deposited at the Li/SEI interface, the R_{SEI} is used to describe the deposition kinetics of Li under this pathway. While deposition at Li/electrolyte interface, the interfacial charge transfer is important. Therefore, Cui's team developed a method called transient cyclic voltammetry. In the voltammogram, the intrinsic exchange current density of charge transfer ($j_0^{c.t.}$) is directly related to the low overvoltage slope. Li charge transfer kinetics can be parameterized by $j_0^{c.t.}$ under this pathway. Deposition kinetics parameterized by R_{SEI} and $j_0^{c.t.}$ are related to the CE of the electrolyte. The results in Figs. 1a and b show that CE is more relevant to $j_0^{c.t.}$ than R_{SEI}. According to previous reports, weakly solvated or Li^+-combined anions increased the $j_0^{c.t.}$ [19]. Therefore, weak solvated electrolytes plate Li uniformly with higher CE. However, it is still necessary to prove the relationship between weak solvation and Li deposition morphology.

The results of the dimensionless analysis of the interface dynamics and ion transport in the electrolyte measured in Figs. 1a and b are contrary to the predictions of the gold standard model of metal deposition. As shown in Figs. 1c and d, when the interfacial resistance R_{SEI} is compared with the electrolyte solution impedance (R_s), there is no correlation between R_{SEI}/R_s and CE (Fig. 1c), while R_{ct}/R_s and CE are negative correlation ($j_0^{c.t.}$ and R_{ct} can be converted by formula) (Fig. 1d). Because there is no trend in R_{SEI}/R_s, many fluorinated and ether electrolytes with high CE are in a state of low R_{ct}/R_s. Therefore, it can be ruled out that different ionic conductivities or Li concentration gradients are the main driving factors for the differences in Li deposition morphology in different electrolytes. Thus, this confirms that the conductivity of some fluorinated ether electrolytes is lower than that of ester electrolytes, but can achieve uniform Li deposition and high CE.

The weak Li^+ solvation not only increases the $j_0^{c.t.}$, but also increases the Li/Li^+ equilibrium potential ($E_{eq.}^{Li/Li+}$), which can facilitate uniform Li morphology and high CE. $E_{eq.}^{Li/Li+}$ is related to the free energy of Li^+ solvation, while the electrolyte of Li^+ weak solvation makes $E_{eq.}^{Li/Li+}$ positive shift. This is associated with two factors as follows: Firstly, the zero-charge potential (φ_{pzc}) has little change in solvent, and the surface charge density (σ) in electrolytes with weak solvation of Li^+ is bigger than that in electrolytes with stronger solvation. This can minimize surface charge fluctuation and prevent dendrite growth. Secondly, the correction of $E_{eq.}^{Li/Li+}$ can also regulate the surface energy (γ) to generate a thermodynamic driving force to achieve more uniform Li deposition. Figs. 1e and f represent three representative electrolytes: lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate/diethylcarbonate (EC/DEC), lithium bis(fluorosulfonyl)imide (LiFSI) in fluoroethylene carbonate (FEC), and LiFSI in a fluorinated derivative of 1,2-dimethoxyethane (F5DEE). When the CE of electrolyte is high, the $E_{eq.}^{Li/Li+}$ value is relatively large. The results show that the F5DEE electrolyte has weak solvation and high CE, so it also has the largest positive σ, which minimizes surface charge fluctuations and increases the surface energy of uniform Li deposition.

Evaluating the early stage of Li electroplating on Cu current collectors can also confirm the main influence of surface energy on Li speciation. According to the classical nucleation theory, the surface energy depends on the nucleation critical radius (r_{crit}) and the nucleation overpotential (η_{nuc}). By measuring the radii of Li particles deposited on Cu foil in different electrolytes, it is found that the particle size of Li is about 85 nm in EC/DEC and 132 nm in F5DEE, and with a median value of 108 nm in FEC (Fig. 2a). η_{nuc} was calculated from the voltage curve shown in Fig. 2b. The particle radius was used as a rough estimate of r_{crit} trend. The results show that the relative surface energy decreases from F5DEE > FEC > EC/DEC

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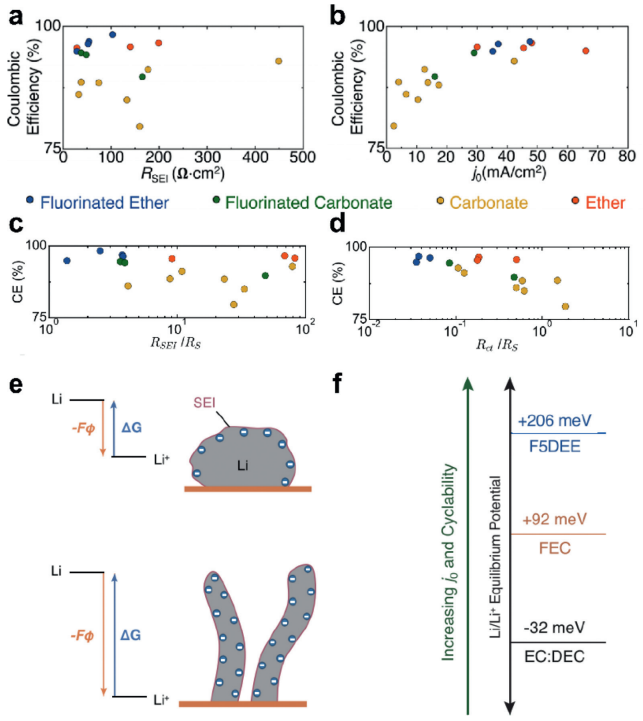

Fig. 1. (a) Relationship between R_{SEI} and CE in different electrolytes. (b) Relationship between $j_0^{c.t.}$ and CE in different electrolytes. (c) Relationship between the electrolyte CE and R_{SEI}/R_S. (d) Relationship between electrical rotor CE and R_{ct}/R_S. (e) Schematic of the proposed model where weak solvation in electrolytes with high $j_0^{c.t.}$ induces higher surface energies of Li and favors electroplating of bulky uniform Li morphology. Schematic of the opposite case where strong solvation favors high surface area plating. (f) Comparison of $E_{eq.}^{Li/Li+}$ obtained from potentiometric measurements of solvation energy in three representative electrolytes: 1 mol/L $LiPF_6$ in EC/DEC, 1 mol/L LiFSI in FEC, and 1.2 mol/L LiFSI in F5DEE. Reprinted with permission [18]. Copyright 2022, American Chemical Society.

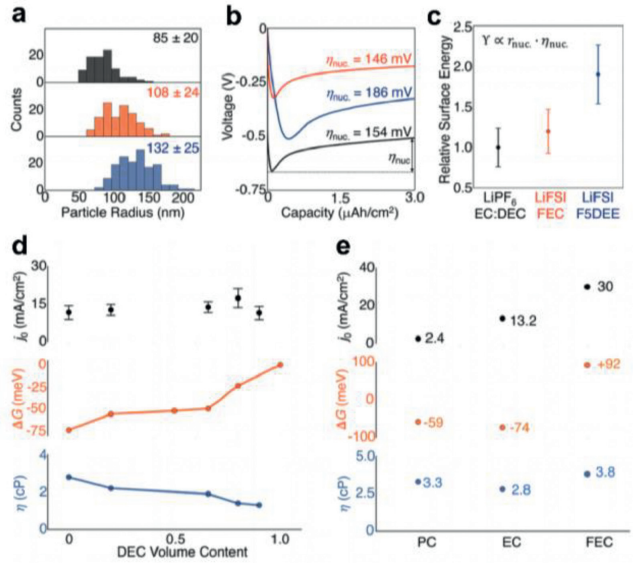

Fig. 2. (a) Distribution of Li particle size in different electrolytes. (b) Voltage distribution for the initial nucleation phase. (c) Relative surface energy is calculated from particle size and η_{nuc}. (d) $j_0^{c.t.}$, the free energy of solvated Li^+, and viscosity η as a function of DEC volume fraction in 1 mol/L LiFSI (EC/DEC) electrolyte. (e) Correlation of $j_0^{c.t.}$, free energy of solvated Li^+ and viscosity in different electrolytes. Reprinted with permission [18]. Copyright 2022, American Chemical Society.

(Fig. 2c). High γ value is favorable for coating larger Li particles, due to the overcome of large η_{nuc}. This indicates that the γ value is the main driving factor of Li speciation. In conclusion, weakly solvated electrolytes make $E_{eq.}^{Li/Li+}$ more positive, and the surface energy is increased, which favors uniform Li deposition.

To further explain the fast $j_0^{c.t.}$ and high surface energy of weakly solvated electrolytes, the molecular factors are considered how to affect the charge transfer kinetics (Figs. 2d and e). The viscosity is found to have little effect on $j_0^{c.t.}$. The charge transfer reaction in battery dynamics is affected by the free energy of the solvated ion and the structure of the bilayer interface. Finally, the extremely weak Li^+ solvation in the fluorinated ether electrolyte shows the best cycling performance. Such weak Li^+ solvation can increase the $j_0^{c.t.}$ and surface energy for favoring bulk low-surface-area Li deposition and high CE.

In short, Cui's work proposes a non-traditional view. They found that weak solvation could shift the $E_{eq.}^{Li/Li+}$ positively and increase the γ of Li for uniform Li deposition, which is different from the traditional view that Li deposition morphology is determined by the ionic conductivity of electrolyte/SEI. Owing to weak solvation, the thermodynamic preference for Li deposition can be adjusted. In the weakly solvated electrolyte, F^-/anion-rich SEI could hinder the crack of the SEI. The SEI fracture as well as ionic conductivity become increasingly important when charged rapidly. Thus, it is recommended to further promote weak Li^+ solvation while improving its ionic conductivity at the same time, by modifying membranes or adding cosolvents/additives. This work provides us insights into exploring functional electrolytes through tuning battery kinetics for future research.

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