



Suspension electrolyte with modified Li⁺ solvation environment for lithium metal batteries

Mun Sek Kim^{1,2,6}, Zewen Zhang^{1,6}, Paul E. Rudnicki², Zhiao Yu^{2,3}, Jingyang Wang^{1,4}, Hansen Wang¹, Solomon T. Oyakhire^{1,2}, Yuelang Chen^{2,3}, Sang Cheol Kim¹, Wenbo Zhang¹, David T. Boyle^{1,3}, Xian Kong^{1,2}, Rong Xu¹, Zhuojun Huang^{1,2}, William Huang¹, Stacey F. Bent², Lin-Wang Wang^{1,4}, Jian Qin^{1,2}, Zhenan Bao^{1,2} and Yi Cui^{1,5}✉

Designing a stable solid-electrolyte interphase on a Li anode is imperative to developing reliable Li metal batteries. Herein, we report a suspension electrolyte design that modifies the Li⁺ solvation environment in liquid electrolytes and creates inorganic-rich solid-electrolyte interphases on Li. Li₂O nanoparticles suspended in liquid electrolytes were investigated as a proof of concept. Through theoretical and empirical analyses of Li₂O suspension electrolytes, the roles played by Li₂O in the liquid electrolyte and solid-electrolyte interphases of the Li anode are elucidated. Also, the suspension electrolyte design is applied in conventional and state-of-the-art high-performance electrolytes to demonstrate its applicability. Based on electrochemical analyses, improved Coulombic efficiency (up to ~99.7%), reduced Li nucleation overpotential, stabilized Li interphases and prolonged cycle life of anode-free cells (~70 cycles at 80% of initial capacity) were achieved with the suspension electrolytes. We expect this design principle and our findings to be expanded into developing electrolytes and solid-electrolyte interphases for Li metal batteries.

Lithium metal (Li⁰) is an ideal anode material due to its low density (0.534 g cm⁻³), high theoretical capacity (3,860 mAh g⁻¹ and 2,061 mAh cm⁻³), low standard electrode potential (-3.04 V versus the standard hydrogen electrode) and compatibility with lithiated and unlithiated cathode materials¹⁻⁴. Achieving stable and reversible Li⁺ migration between the cell electrodes poses a formidable challenge due to the existence of an intricate solid-electrolyte interphase (SEI) at the Li⁰ anode and electrolyte interface⁵. Designing stable SEIs on a Li⁰ anode is the key to success in developing Li⁰ batteries (LMBs) as the properties of SEIs largely dictate the electrochemical performances of the Li⁰ anode⁶⁻⁸. However, the control and understanding of the SEI on the Li⁰ anode remain challenging due to heterogeneous composition⁹, nanostructure⁵, hypersensitivity to the ambient environment^{6,8} and spatiotemporal evolution¹⁰ of the SEIs.

As the SEI evolution on the Li⁰ anode is directly associated with electrolyte formulations, various electrolyte modifications (blending different solvents¹¹⁻¹³ and salts¹⁴, designing new solvents¹⁵, varying salt concentrations¹⁶⁻²⁰ and using solvent-specific diluents²¹⁻²³) have been studied to delineate different SEI properties that influence the electrochemical performances of the Li⁰ anode⁵. The consensus is that the inorganic-rich SEIs on the Li⁰ anode promote superior electrochemical performances¹⁵⁻²³. Since inorganic and organic contents of SEIs were closely linked to the electrolyte Li⁺ solvation environment⁵, understanding and modifying electrolyte Li⁺ solvation structures has become an important driver for developing electrolytes for LMBs.

To date, the pursuit of forming inorganic-rich SEIs has been achieved by increasing Li⁺-anion coordination (maximizing contact ion pairs and ionic aggregates)¹⁶⁻²³ and weakening Li⁺-solvent

coordination (minimizing solvent-separated ion pairs)^{15,24} in the electrolyte Li⁺ solvation shells. The general approaches to increase contact ion pairs and ionic aggregates in the Li⁺ solvation shells are to use high concentration electrolytes (HCEs)¹⁶⁻²⁰ or combine HCEs with solvent-specific diluents to make localized HCEs (LHCEs)¹⁵⁻²³. As the coordination between Li⁺ and solvent is affected by the polarity and/or donor number of solvents^{5,17}, designing a new solvent with functional structures has enabled the decrease in Li⁺-solvent and increase in Li⁺-anion coordinations that create inorganic-rich SEIs on the Li⁰ anode¹⁵.

Herein, we propose a suspension electrolyte design, a mixture of inorganic nanoparticles with liquid electrolytes, to understand the suspension's role in impacting the SEI evolution and the electrochemical performances of the Li⁰ anode. Due to the ubiquitous presence of Li₂O in both prevalent and inorganic-rich SEIs⁵ of the Li⁰ anode and to the low solubility of Li₂O (ref. 25), a Li₂O suspension was scrutinized to elucidate the working mechanism of the Li₂O suspension in the electrolyte and to reveal features of Li₂O that relate to SEIs of the Li⁰ anode. To systematically study the suspension electrolytes, we investigated a reference carbonate electrolyte (RCE; 1 M LiPF₆ in ethylene carbonate (EC)/diethylene carbonate (DEC)/10 vol% fluoroethylene carbonate (FEC)) that is widely studied as a standard electrolyte for the Li⁰ anode and SEIs^{5,7,8,10,26}; a reference fluorinated electrolyte (RFE; 1 M lithium bis(fluorosulfonyl) imide (LiFSI) in fluorinated 1,4-dimethoxybutane (FDMB)) that is one of the state-of-the-art electrolytes with a modified Li⁺ solvation structure¹⁵; and a reference LHCE (RLHCE; 1 M LiFSI in dimethoxyethane (DME)/1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE; 0.78:0.22 v/v)) that exhibits a unique Li⁺ solvation environment²¹. The suspension electrolytes were prepared by adding

¹Department of Materials Science and Engineering, Stanford University, Stanford, CA, USA. ²Department of Chemical Engineering, Stanford University, Stanford, CA, USA. ³Department of Chemistry, Stanford University, Stanford, CA, USA. ⁴Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA, USA. ⁵Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, CA, USA. ⁶These authors contributed equally: Mun Sek Kim, Zewen Zhang. ✉e-mail: yicui@stanford.edu

~80–100 nm Li_2O nanoparticles into RCE, RFE and RLHCE, which were then referred to as the suspension carbonate electrolyte (SCE), suspension fluorinated electrolyte (SFE) and suspension LHCE (SLHCE), respectively. Through theoretical and empirical analyses on the Li_2O suspension electrolyte, several key features of Li_2O were identified: (1) Li_2O modifies the Li^+ solvation environment through the interfacial interactions between the Li_2O surface and its surrounding Li^+ solvation shells of the liquid electrolyte, (2) Li_2O creates a weakly solvating environment by decreasing Li^+ –solvent and increasing Li^+ –anion coordinations, (3) Li_2O facilitates desolvation of solvated Li^+ , (4) Li_2O attracts fluorinated species and dissociated Li^+ , (5) Li_2O induces inorganic-rich and anion-derived SEIs on the Li^0 anode, (6) Li_2O promotes a formation of temporally and electrochemically stable interphases on the Li^0 anode, (7) Li_2O suppresses dendritic growth of Li^0 and (8) Li_2O is a beneficial inorganic material for the Li^0 anode. Importantly, these findings help to explain previously reported improved Li^0 anode performances with the multi-layered Li_2O SEI^{7,8,27,28}. Despite the veiled formation mechanism of multi-layered^{7,8,27,28}, amorphous³⁹ and crystalline^{30–32} Li_2O in SEIs, increasing Li_2O content in SEIs improves the Li^+ migration stability of the Li^0 anode^{7,8,27–32}, a result in which the previous findings agree with the outcome of this study. We demonstrate an improved Coulombic efficiency (CE) of ~99.7% for Li^0 and electrochemical performances of anode-free full cells with the suspension electrolyte design. As a corollary, the suspension electrolyte design adds extra layers to the fundamental understanding of the inorganics in SEIs (that is, Li_2O), provides a comprehensive electrolyte engineering strategy and guides the development of electrolytes for LMBs.

Analyses of the suspension electrolyte

The SEI evolution of Li^0 depends on the Li^+ solvation environment of electrolytes and solubility of decomposed electrolyte species (Supplementary Note 1). We found that the major impact of the Li_2O suspension electrolyte originates from the modification of the Li^+ solvation environment in the vicinity of the Li_2O surface. Therefore, one of the criteria for optimizing the suspension electrolyte effect is to have the suspension laying out near the surface of the Li^0 anode to affect the SEI evolution. Furthermore, we hypothesize that saturating Li_2O in the suspension electrolyte is also a contributing factor that impacts the SEI evolution of the Li^0 anode as Li_2O is least soluble, but not completely insoluble, in electrolytes²⁵, among the prevalent inorganics (Li_2O , Li_2CO_3 and LiF) observed in SEIs of the Li^0 anode⁷. By synthesizing the previous findings and key results from this work, we portray SEI evolutions on the Li^0 anode with liquid and suspension electrolytes in Fig. 1a,b. Figure 1a (Supplementary Fig. 1) depicts the SEI evolution of a conventional liquid electrolyte (Supplementary Note 2) on a Li^0 anode that forms an organic-rich SEI, while Fig. 1b (Supplementary Fig. 2) interprets the altered SEI evolution on a Li^0 anode induced by the modified Li^+ solvation environment in the Li_2O suspension electrolyte (Supplementary Note 3), which creates an inorganic-rich SEI on the Li^0 anode.

To access the electrochemical features of the RCE and SCE, the CE measurements³³ from $\text{Li}|\text{Cu}$ cells were conducted (Fig. 1c). The CE of SCE (97.5%) exhibited an ~4% increase relative to that of RCE (93.4%). The nucleation overpotentials^{34,35} for RCE (99.5 mV) and SCE (41.2 mV) were also calculated (Fig. 1c), in which SCE exhibited a lower energy barrier to form Li^0 nuclei. Averaged CEs and nucleation overpotentials with standard errors are reported in Fig. 1d. It is apparent that the improved CE and reduced nucleation overpotential with SCE arise from the Li_2O suspension, as the identical liquid electrolyte was used for RCE and SCE. The major determinants of CEs are correlated with topography¹⁰ of Li^0 electrode deposits and SEI characteristics⁷. The scanning electron microscopy (SEM) images in Fig. 1e,f provide a clear physical insight into the morphological features of Li^0 electrode deposits on Cu with RCE and

SCE. The resulting morphologies with RCE exhibited high surface area and dendritic Li^0 electrode deposits on Cu (Fig. 1e), which is a common signature of standard carbonate-based electrolytes^{7,8,26}. On the contrary, denser and bulkier Li^0 electrode deposits on Cu were observed with SCE (Fig. 1f). The lower surface area and bulkier Li^0 electrode deposits obtained with SCE (Fig. 1f) compared with RCE (Fig. 1e) explain the improvement of the CE and reduced nucleation overpotential. It is known that a substantial number of charges are consumed irreversibly to form SEIs on a Li^0 anode surface, indicating an inversely proportional relationship between CE and the surface area of Li^0 electrode deposits^{1,33}. Furthermore, a smaller nucleation overpotential thermodynamically favours forming larger sizes of Li^0 nuclei, eventually leading to bulkier Li^0 electrode deposits³⁵. Thus, the lower surface area and bulkier Li^0 electrode deposits achieved with SCE (Fig. 1f) than with RCE (Fig. 1e) support CE improvement and reduced nucleation overpotential (Fig. 1c,d).

To investigate the nanoscopic origin of the performance enhancement of SCE, we utilized cryogenic scanning transmission electron microscopy (cryo-STEM)^{6,8} to probe the nanostructure and local chemistry of the compact SEI derived from RCE (RCE-SEI) and from SCE (SCE-SEI). The Li^0 electrode deposits on the Cu transmission electron microscopy (TEM) grid with RCE (Fig. 2a) and SCE (Fig. 2b) confirm the consistent Li^0 morphology observed in Fig. 1e,f. The high-resolution cryo-TEM images of RCE-SEI (Fig. 2c) and SCE-SEI (Fig. 2d) reveal the thinner and Li_2O -richer (Supplementary Fig. 1) characteristics of SCE-SEI.

Cryo-STEM electron energy loss spectroscopy (EELS) was performed to identify the differences in the chemistries of RCE-SEI and SCE-SEI. In the oxygen K-edge map, a more abundant distribution of oxygen elements was identified for SCE-SEI (Fig. 2e,f). Moreover, carbon K-edge (Fig. 2g) and oxygen K-edge (Fig. 2h) fine structures of RCE-SEI and SCE-SEI were compared to delineate the SEI chemistries. For SCE-SEI, a lower C–H signal (around 286 eV) and higher C=O signal (around 290 eV) were obtained relative to RCE-SEI^{6,10}. The lower C–H and higher C=O signals in the carbon K-edge fine structure of SCE-SEI signify relatively lower organic content in SCE-SEI than in RCE-SEI^{6,10}. This claim was further evidenced by observing the oxygen K-edge fine structure in Fig. 2h. The absence of the peak around 531 eV in the oxygen K-edge fine structure (Fig. 2h) of SCE-SEI indicates the Li_2O -dominated SEI chemistry^{6,36}, in which the result matches with the abundant Li_2O observed in Supplementary Fig. 1b. Based on the cryo-STEM and EELS analyses, SCE-SEI was inorganic rich, particularly in Li_2O . The enrichment of Li_2O in SCE-SEI is corroborated in Supplementary Note 4 and Supplementary Fig. 2. We also speculate that the different morphological features of Li^0 electrode deposits with RCE and SCE (Figs. 1e,f and 2a,b) are possibly related to the high surface energy of Li_2O in SEIs (Supplementary Fig. 3), as the high-surface-energy SEI has been known to suppress the formation of Li^0 dendrites³⁷ (Supplementary Note 5). The different evolution of SEIs observed with RCE and SCE strongly suggests that the Li^+ solvation environment in RCE and SCE must be different due to an interplay between the SEI evolution on Li^0 and in the Li^+ solvation environment of electrolytes⁵.

Li^+ solvation environment of the suspension electrolyte

Molecular dynamics (MD) simulations were conducted to understand the Li^+ solvation environment in RCE and SCE, which impacts the SEI formation on the Li^0 anode⁷ (Fig. 3). Snapshots of simulated RCE and SCE systems are shown in Fig. 3a, and the normalized density profiles of the electrolyte species in SCE are plotted in Fig. 3b. Near the Li_2O slab in SCE, the Li^+ solvation structure differs from that observed in RCE, as evidenced by clear peaks in the normalized density profile due to the strong adsorption and diffusion of Li^+ at the Li_2O surface and the different coordination of electrolyte components to the Li_2O surface (Fig. 3c). Furthermore,

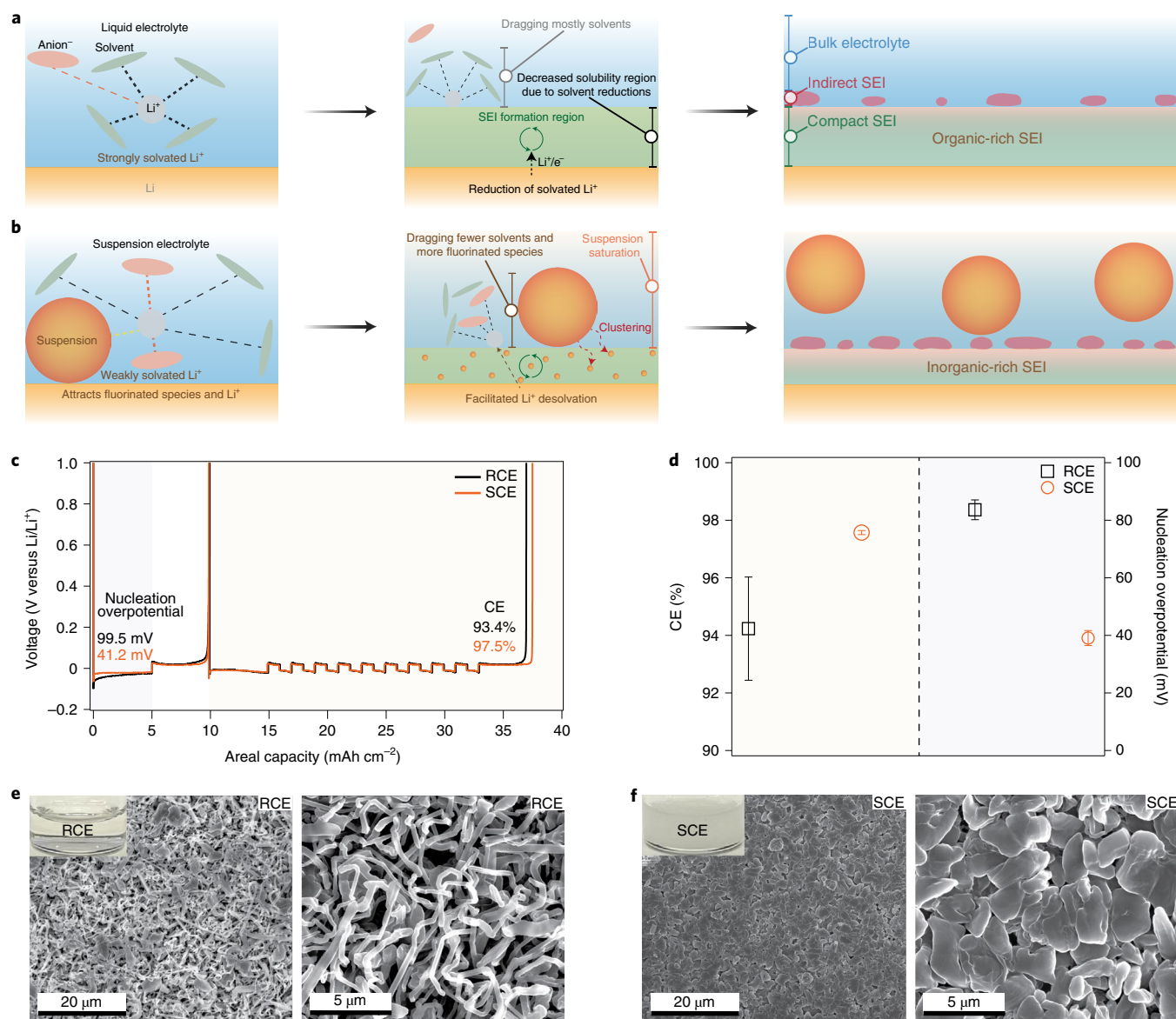


Fig. 1 | Liquid and suspension electrolytes for the Li⁰ anode. a, Schematic illustration for a conventional liquid electrolyte affecting the SEI evolution of the Li⁰ anode. The details for each of the subset schematics are provided in Supplementary Figure Caption 1. e⁻, electron. **b**, Schematic illustration for a suspension electrolyte affecting the SEI evolution of the Li⁰ anode. The details for each of the subset schematics are provided in Supplementary Figure Caption 2. **c**, Representative voltage profiles from Li|Cu cells with RCE and SCE for measuring CE and nucleation overpotential at 0.5 mA cm⁻². The background colours represent where the CE and nucleation overpotential were calculated. **d**, Averaged CE and nucleation overpotential values from four identical Li|Cu cells with RCE and SCE. The background colours represent the regions where CE and nucleation overpotential were calculated from **c**. The averaged CE and nucleation overpotential values of the electrolytes with standard errors are RCE (94.23 ± 1.79% and 83.65 ± 3.43 mV) and SCE (97.57 ± 0.07% and 39.10 ± 2.61 mV). The error bars were calculated by taking the standard errors from the measurements with four identical samples. **e**, Low (left) and high (right) magnification SEM images of Li⁰ electrodeposit on Cu from the Li|Cu cell with RCE at 1 mA cm⁻² and 1 mAh cm⁻². The inset image shows the physical image of RCE. **f**, Low (left) and high (right) magnification SEM images of Li⁰ electrodeposit on Cu from the Li|Cu cell with SCE at 1 mA cm⁻² and 1 mAh cm⁻². The inset image shows the physical image of SCE.

density functional theory (DFT) calculations were performed to figure out the most favourable Li adatom interaction sites for the Li₂O(111) surface. According to Fig. 3d, Li₂O(111) surface site 1 (-0.93 eV) provided the most favourable Li adatom adsorption, demonstrating a favoured Li⁰-O_{Li₂O} interaction, where O_{Li₂O} is the oxygen in Li₂O (Supplementary Note 6). These simulation results revealed the existence of Li^{0/+}-Li₂O interactions that could influence the Li⁺ solvation environment. Moreover, FEC also showed a larger concentration near the Li₂O surface relative to EC. Density profiles of electrolyte species in RCE and away from the Li₂O surface

in SCE exhibited a similar behaviour (Supplementary Fig. 4). In other words, the effect of Li₂O suspension comes from the interfacial interaction between Li₂O and its neighbour Li⁺ solvation shells of the liquid electrolyte.

Radial distribution functions (RDFs) were used to analyse the relative compositions of electrolyte species in the first Li⁺ solvation shell of SCE (Fig. 3e) and RCE (Fig. 3f). The fluorinated species (FEC and PF₆⁻) were enriched in the first Li⁺ solvation shell of SCE relative to the non-fluorinated carbonates (EC and DEC), while RDFs of Li⁺ farther from the Li₂O surface exhibited similar

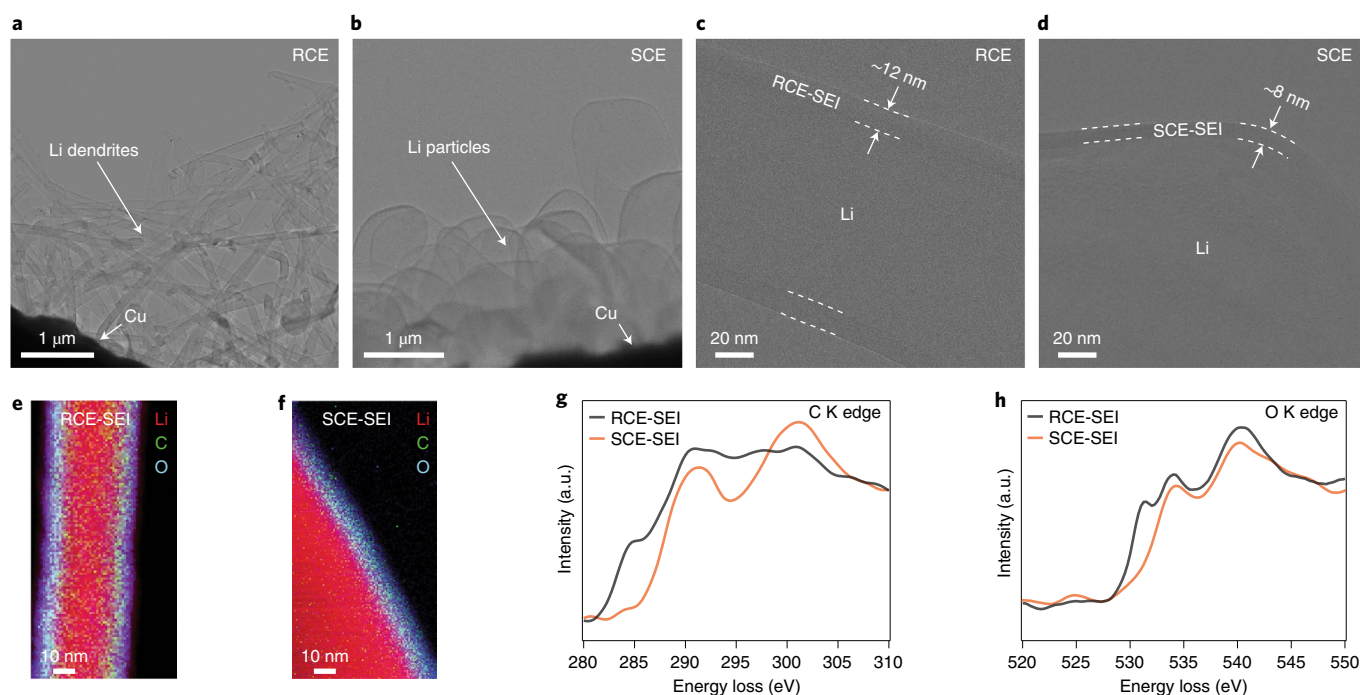


Fig. 2 | Compact SEI analysis via cryo-STEM. **a, b**, Low magnification cryo-STEM images of Li^0 electrodeposits on Cu TEM grid with RCE (**a**) and SCE (**b**). The samples were prepared from a Li/Cu -TEM-grid cell at 1 mA cm^{-2} and 0.1 mAh cm^{-2} . The arrows indicate the morphology of the Li^0 electrodeposit with RCE and SCE. **c, d**, High magnification cryo-STEM images of RCE-SEI (**c**) and SCE-SEI (**d**). SEI regions and the thicknesses are illustrated with dashed lines and arrows. **e, f**, Large area cryo-STEM EELS mapping of Li (red), C (green) and O (sky blue) around RCE-SEI (**e**) and SCE-SEI (**f**). **g**, Carbon K-edge fine structure of RCE-SEI and SCE-SEI obtained from EELS. **h**, Oxygen K-edge fine structure of RCE-SEI and SCE-SEI obtained from EELS.

characteristics to those in RCE (Supplementary Fig. 5). This is quantified by examining the composition of the first Li^+ solvation shell in each environment, revealing that both FEC and PF_6^- were increased by percentage in the first Li^+ solvation shell near the Li_2O surface in SCE, while EC was more prevalent in the Li^+ solvation shells of RCE (Fig. 3g and Supplementary Fig. 6). The molecular origin of the fluorinated species enrichment at the Li_2O surface is explained in Supplementary Note 7 with Supplementary Figs. 7 and 8. Consequently, the enrichment of fluorinated species in the Li^+ solvation shells near the Li_2O surface explains the increased content of LiF and F/O counterparts, which promotes stable Li^+ migration^{5,38}, observed around Li_2O in SEIs of the Li^0 anode due to the preferential decomposition of fluorinated species^{26,30}. Also, these results verify the desirable features of the multi-layered Li_2O SEIs observed in previous works^{7,8,27,28}. Overall, three essential features of the Li_2O in the electrolyte were revealed by the simulations: (1) the Li^+ solvation environment changes (more anion and less solvent to Li^+ coordinations) near the surface of Li_2O , (2) the fluorinated species are enriched near the surface of Li_2O and (3) dissociated Li^+ in the electrolyte is strongly adsorbed onto the Li_2O surface.

The relative solvation energies of RCE and SCE were measured with an H-cell³⁹ comprised of symmetric Li^0 electrodes but asymmetric electrolytes to experimentally verify the features of Li_2O attained from the simulations (Supplementary Note 8). Based on the solvation energy measurements with RCE and 20 wt% Li_2O SCE (Fig. 4a), a smaller cell potential (E_{cell}) and more positive solvation energy were measured with 20 wt% Li_2O SCE. This trend signifies that dissociated Li^+ in 20 wt% Li_2O SCE became relatively weakly solvated. In other words, the Li_2O suspension in the electrolyte decreases the Li^+ -solvent coordination (facilitating desolvation of Li^+ in the solvation shell) and increases the Li^+ -anion coordination (promoting anion-derived SEIs on the Li^0 anode)³⁹. Furthermore, the solvation energies were measured with a larger Li_2O particle

(a Li_2O microparticle) but equal weight percent in the electrolyte to examine the effect of the surface-area-to-volume ratio of the Li_2O suspension (Supplementary Fig. 9). The same E_{cell} and solvation energy trends were detected with 20 wt% Li_2O microparticle; however, the change was smaller in magnitude (Supplementary Note 9). This substantiates that the Li^+ solvation environment change depends on the surface-area-to-volume ratio of the Li_2O suspension in the electrolyte, which shows that the modification of the Li^+ solvation environment arises from the surface interactions of Li_2O . Thus, the solvation energy measurements experimentally proved the features of Li_2O obtained from the simulation results (Supplementary Note 10).

The ^7Li NMR analysis⁴⁰ provides two important characteristics about the suspension electrolyte: (1) qualitatively confirming the altered Li^+ solvation environment in the suspension electrolyte and (2) determining the optimal suspension content in the suspension electrolyte. The ^7Li NMR spectra of RCE, 1–20 wt% Li_2O SCE and 7 wt% Li_2O in EC/DEC are shown in Fig. 4a. The upfield (shifting to lower parts per million, to the right) or downfield (shifting to higher parts per million, to the left) peak shifts describe the changes in the Li^+ solvation environment: the upfield and downfield peak shifts represent increased and decreased electron density around the nuclei of dissociated Li^+ , respectively⁴⁰. In Fig. 4a, the peak of SCE as a function of Li_2O content gradually shifts to the upfield direction (increasing electron density of the solvated Li^+) as the Li_2O suspension content increases. The upfield peak shifts, therefore, reflect increased Li^+ coordination with negatively charged species in the electrolyte. The simulation results (Fig. 3) and the solvation energy trend (Fig. 4a) illustrate that the upfield peak shifts stem from the increased Li^+ -anion coordination, while Li^+ -solvent coordination was relatively weakened. Also, the Li^+ density profile in Fig. 3c shows the surface adsorption of Li^+ onto Li_2O , in which the Li^+ - $\text{O}_{\text{Li}_2\text{O}}$ interaction contributes to the upfield peak shifts as the oxygen

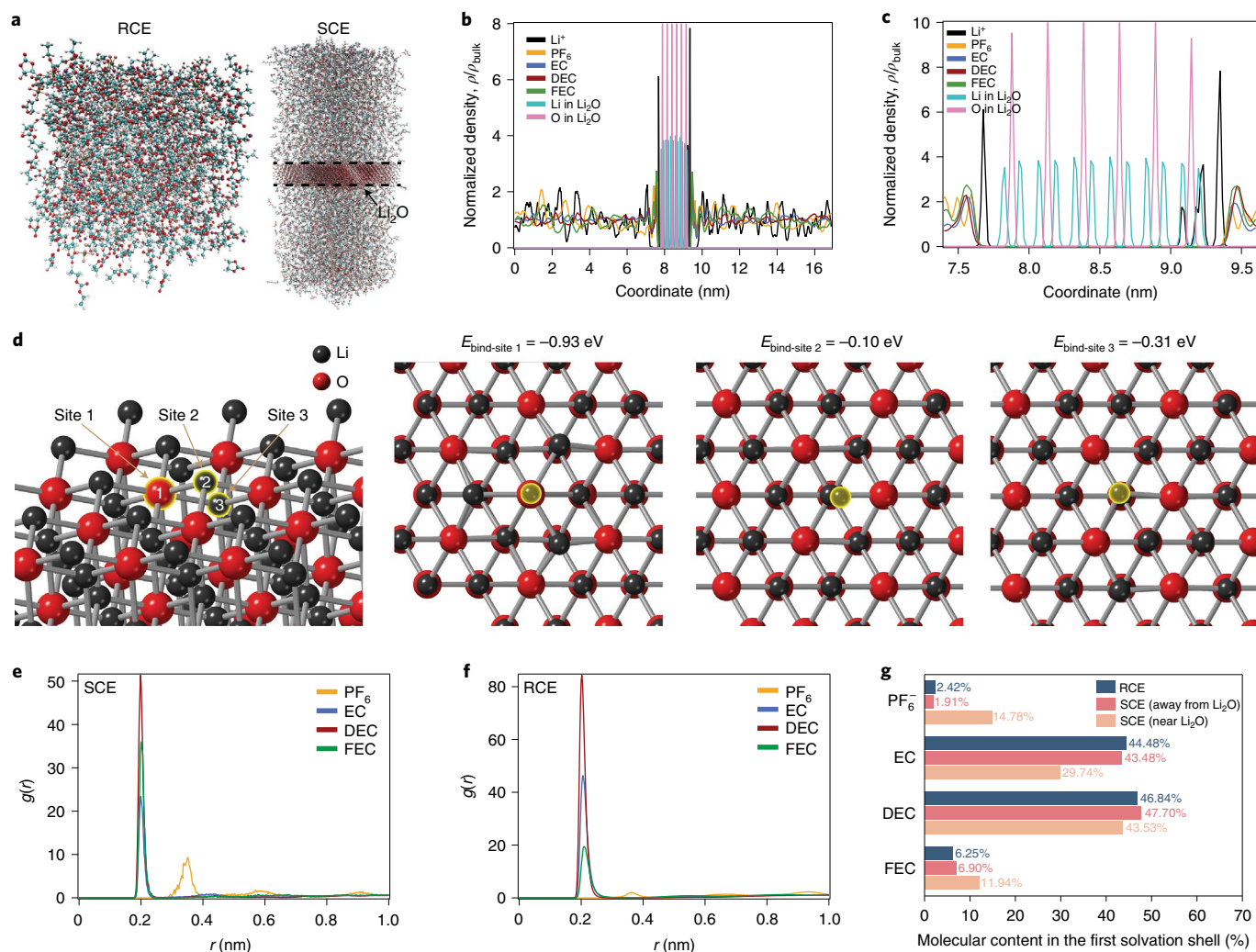


Fig. 3 | Simulations for the Li⁺ solvation environment of RCE and SCE. **a**, Snapshots of MD simulations of molecular species (Li⁺, PF₆⁻, EC, DEC and FEC) for RCE and SCE. The colour codes for the images are oxygen (red), carbon (cyan), hydrogen (white), phosphorus (tan), fluorine (pink), Li⁺ (purple) and Li in Li₂O (grey). **b**, Density profiles of SCE with the Li₂O slab. The ρ and ρ_{bulk} represent density and bulk density of the specified species. **c**, Density profiles of SCE near the Li₂O slab in **b**. **d**, Snapshots of Li adatom binding sites 1 to 3 on the Li₂O(111) surface. Sites 1, 2 and 3 refer to the Li adatom adsorbed close to the oxygen on the Li₂O surface, the Li adatom adsorbed to the outward lithium on the Li₂O surface and the Li adatom adsorbed to the inward lithium on the Li₂O surface, respectively. The DFT-calculated binding energies of the Li adatom on site 1, site 2 and site 3 ($E_{\text{bind-site } 1}$, $E_{\text{bind-site } 2}$ and $E_{\text{bind-site } 3}$, respectively) were -0.93 eV, -0.10 eV and -0.31 eV, respectively. **e**, RDFs for the first Li⁺ solvation shell of SCE near the Li₂O slab. The $g(r)$ represents the radial distribution function. **f**, RDFs for the first Li⁺ solvation shell of RCE. **g**, Calculated electrolyte species content in the first Li⁺ solvation shell in the bulk of RCE and away from and near the Li₂O slab of SCE.

is negatively charged. Furthermore, the peak shifts as a function of the Li₂O suspension content in the electrolyte emphasize that the degree of the change in the Li⁺ solvation environment depends on the absolute surface area and the surface-area-to-volume ratio of the Li₂O suspension in the electrolyte (Supplementary Note 11 with Supplementary Fig. 10). Note that the absence of the peak in the spectra of 7 wt% Li₂O in EC/DEC (Fig. 4b) confirms that the observed Li⁺ peaks in RCE and 1–20 wt% Li₂O SCE were the dissociated Li⁺ from the salt, not Li₂O suspension (Supplementary Note 12 with Supplementary Fig. 11). The amount of relative upfield peak shift is linear in suspension contents up to 7 wt% and increases steadily beyond 7 wt% (Fig. 4c), indicating that the effects of suspension on the Li⁺ solvation environment is weakened above 7 wt% of Li₂O loading (Supplementary Note 13 with Supplementary Fig. 12). Therefore, 7 wt% Li₂O is considered as the optimal content for SCE and has been employed to measure the electrochemical properties of SCE. These Li⁺ solvation environment analyses reveal that

the Li⁺ solvation environment gets modified near the surface of the Li₂O suspension in the electrolyte. Moreover, this mechanism suggests that it is crucial to have the Li₂O suspension in the vicinity of the Li⁰ anode to deliver the effects; the Li₂O suspension effects are further discussed in Supplementary Note 14 with Supplementary Figs. 13 and 14.

Li⁰ interphases with the suspension electrolyte

X-ray photoelectron spectroscopy (XPS) surface analysis on electrodeposited Li⁰ was performed to extract more information about the indirect SEI (iSEI) region as XPS has high out-of-plane resolutions²⁶. The elemental ratios of P/C, F/C, F/O and C/O, which help to track the origin of the sources to construct iSEIs (Supplementary Note 15), from iSEI with RCE (RCE-iSEI) and with SCE (SCE-iSEI) were calculated (Fig. 4d). Relatively higher P/C, F/C and F/O ratios and a lower C/O ratio were obtained for SCE-iSEI compared to that for RCE-iSEI. These ratios confirm that more anions were

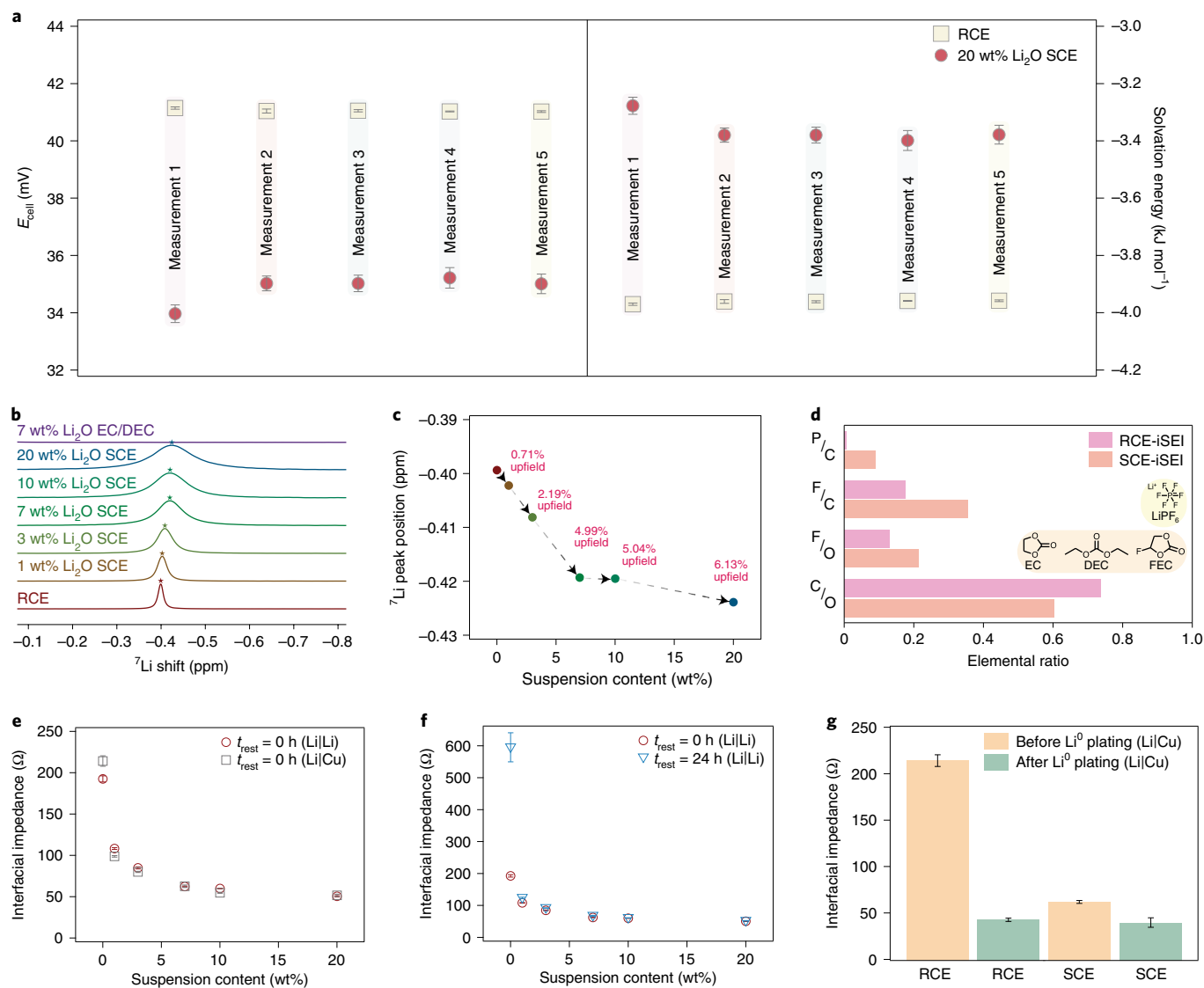


Fig. 4 | Further analysis of the suspension electrolyte. **a**, The potentiometric measurements of averaged cell potentials (E_{cell} , left half) and Li^+ solvation energies (right half) with standard errors for RCE and 20 wt% Li_2O SCE. **b**, The ^7Li NMR spectra of RCE and 1 wt% to 20 wt% Li_2O SCE. **c**, The ^7Li NMR peak positions retrieved from **b** with respect to the suspension contents. The relative peak shifts are indicated with the arrows. **d**, Elemental ratios of P/C, F/C, F/O and C/O on RCE-iSEI and SCE-iSEI obtained from XPS scans. The XPS scans were performed on electrodeposited Li^0 on Cu from Li|Cu cells with RCE and SCE at 1 mA cm^{-2} and 1 mAh cm^{-2} . The insets represent electrolyte species that can be reduced to form iSEIs on the Li^0 anode. **e**, The interfacial impedance of Li|Li and Li|Cu cells with RCE and 1 wt% to 20 wt% SCE measured at $t_{\text{rest}} = 0\text{ h}$. The t_{rest} value represents the cell resting time after cell assembly. **f**, The interfacial impedance of Li|Li cells with RCE and 1 wt% to 20 wt% SCE measured at $t_{\text{rest}} = 0\text{ h}$ and $t_{\text{rest}} = 24\text{ h}$. **g**, The interfacial impedance measured before and after Li^0 electrodeposition on Cu from Li|Cu cells with RCE and SCE at 1 mA cm^{-2} and 1 mAh cm^{-2} . Three identical samples were measured in **e**, **f** and **g** to obtain the averaged interfacial impedance values with standard errors.

decomposed in SCE-iSEI than the solvents, which agrees with the characteristics of the modified Li^+ solvation in SCE (Figs. 3 and 4a,b)^{5,17} and validates higher contents of inorganic species in SCE-iSEI on Li^0 . The high-resolution XPS spectra of P, C, O and F (Supplementary Fig. 15) revealed higher Li_2O and LiF contents for SCE-iSEI than for RCE-iSEI. Additionally, it has been reported that Li_2O in SEIs can act as a conduit for electron transfer as it is more receptive to electronic charge transfer from the Li^0 anode. The transferred electrons then participate to preferentially decompose anions that favour anion-derived species in SEIs on the Li^0 anode⁴¹.

The electrochemical impedance spectroscopy of Li^0 electrodes was measured with RCE and ~ 1 –20 wt% Li_2O SCE (Fig. 4e,f) to evaluate the characteristics of the interphases that Li^0 forms with the Li_2O suspension in the electrolyte. Collectively, Li|Li and Li|Cu cells

were used to systematically verify the interfacial impedance trends (Fig. 4e, Supplementary Fig. 16 and Supplementary Table 1). A noticeable decrease of the interfacial impedances was observed with ~ 1 –20 wt% Li_2O SCE. The decrease of the interfacial impedance is attributed to the weakly solvating environment that may facilitate Li^+ desolvation induced by the Li_2O suspension in the electrolyte (Fig. 4a) and promoted surface adsorption of Li^+ onto the Li_2O surface (Fig. 3c). Also, the features of Li_2O -rich³⁰ SCE-SEI (Fig. 2f,h and Supplementary Fig. 1), inorganic-rich SCE-iSEI (Fig. 4d) and thin SCE-SEI (Fig. 2d) further support the decrease of the interfacial impedance of Li^0 with SCE. More importantly, the magnitude of the interfacial impedance decrease per Li_2O suspension content in SCE was different, exhibiting a minor decrease in the interfacial impedance of Li^0 above 7 wt% Li_2O SCE (Fig. 4e). As the Li^+

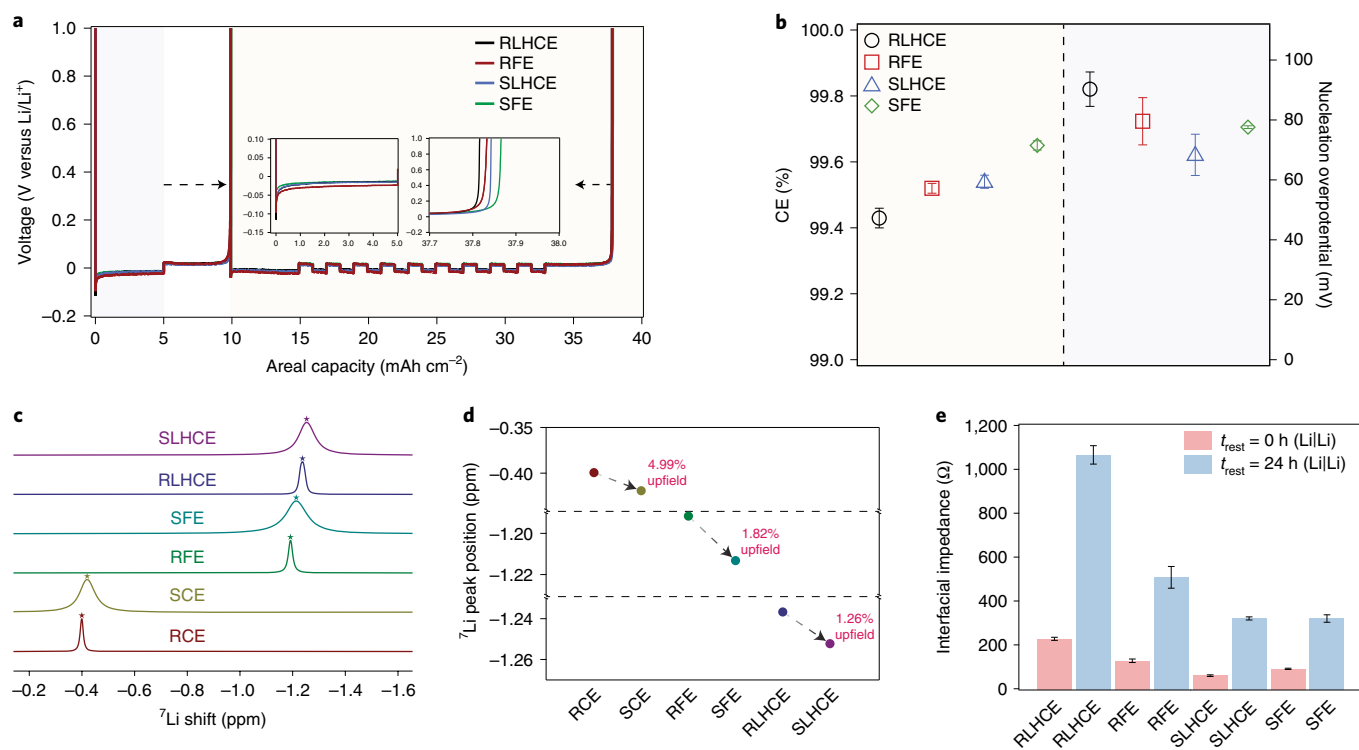


Fig. 5 | High-performance electrolytes with the suspension electrolyte design. **a**, Representative voltage profiles from Li|Cu cells with RLHCE, RFE, SLHCE and SFE for measuring CE and nucleation overpotential at 0.5 mA cm^{-2} . The insets show magnified initial and final voltage profiles to express clearer comparisons among the tested electrolytes. **b**, Averaged CE and nucleation overpotential values from four identical Li|Cu cells with RLHCE, RFE, SLHCE and SFE. The background colours represent the regions where CE and nucleation overpotential were calculated from **a**. The averaged CE and nucleation overpotential values of the electrolytes with standard errors are RLHCE ($99.43 \pm 0.03\%$ and $90.27 \pm 5.75 \text{ mV}$), RFE ($99.52 \pm 0.015\%$ and $79.57 \pm 7.87 \text{ mV}$), SLHCE ($99.54 \pm 0.02\%$ and $68.37 \pm 6.88 \text{ mV}$) and SFE ($99.65 \pm 0.014\%$ and $77.63 \pm 0.47 \text{ mV}$). **c**, The ^7Li NMR spectra of RCE, SCE, RFE, SFE, RLHCE and SLHCE. **d**, The ^7Li NMR peak positions retrieved from **c** for RCE, SCE, RFE, SFE, RLHCE and SLHCE. The relative peak shifts are indicated with the arrows between the points. **e**, The interfacial impedance of Li|Li cells with RLHCE, RFE, SLHCE and SFE measured at $t_{rest} = 0 \text{ h}$ and $t_{rest} = 24 \text{ h}$. The t_{rest} value represents the cell resting time after cell assembly. Three identical samples were measured to obtain averaged interfacial impedance values with standard errors.

solvation environment was affected by the Li_2O suspension content (Fig. 4a–c and Supplementary Figs. 9 and 10), the interfacial impedance decrease (Fig. 4e) based on the Li_2O suspension content was in line with the Li^+ solvation environment changes observed in ^7Li NMR (Fig. 4b,c).

Moreover, monitoring temporal characteristics of interphases formed with a particular electrolyte on Li^0 became crucial due to the ageing of Li^0 , which results in increased interfacial impedances of the Li^0 anode over time¹⁰. Thus, the interfacial impedances of Li^0 were measured with RCE and ~1–20 wt% Li_2O SCE after 24 hours of cell assembly with respect to the suspension contents (Fig. 4f, Supplementary Fig. 17 and Supplementary Table 2). The change of the interfacial impedance in the suspension electrolytes became a weak function of time, indicating stable temporal characteristics of the interphases of Li^0 formed with SCE. Furthermore, the magnitude of the change in the interfacial impedance became smaller above 7 wt% Li_2O , which supports the optimal suspension content and thereby the optimal Li^+ solvation change effect, observed in Fig. 4b,e. Nyquist plots (Supplementary Fig. 17) for the impedance measurements in Fig. 4f demonstrate that electrolyte conductivity does not change with time, further supporting the stability of SCE and the interphases of Li^0 formed with SCE.

For the electrodes involving reactive materials such as Li^0 , the large variation in the interfacial impedance after the electrochemical processes suggests that the system undergoes a more dynamic evolution and potentially unstable electrochemical processes. To illustrate this point, the interfacial impedances were measured from

Li|Cu cells before and after Li^0 electrodeposition with RCE and SCE (Fig. 4g, Supplementary Fig. 18 and Supplementary Table 3). The change of the interfacial impedance after Li^0 electrodeposition was smaller for SCE than for RCE (Fig. 4g). To corroborate the electrochemical stability during the Li^+ migration, the voltage responses deduced from the repeated galvanostatic Li^0 plating/stripping with RCE and SCE certify that SCE allowed more stabilized Li^+ migration as less voltage hysteresis was achieved with SCE than with RCE (Supplementary Fig. 19).

Suspensions in high-performance electrolytes

We further extended the suspension electrolyte design to validate its effect on the high-performance electrolytes (RFE and RLHCE). The CE measurements were performed with RLHCE, RFE, SLHCE and SFE to observe the CE and nucleation overpotential (Fig. 5a). The averaged values of CE and nucleation overpotential for the electrolytes are summarized in Supplementary Table 4. Both SFE and SLHCE exhibited improved CEs and reduced nucleation overpotentials (Fig. 5b), for which the suspension electrolyte design enabled further improvements for the high-performance electrolytes. To vividly portray the CE improvements of the carbonate (RCE) and high-performance electrolytes (RFE and RLHCE) with the suspension electrolyte design, the percent decrease in averaged Coulombic inefficiencies (CI_{avg} decrease) were calculated (Supplementary Note 16 with Supplementary Fig. 20). The Li^0 electrodeposits with SFE (Supplementary Fig. 21) and SLHCE (Supplementary Fig. 22) were examined to understand the improved CE and reduced nucleation

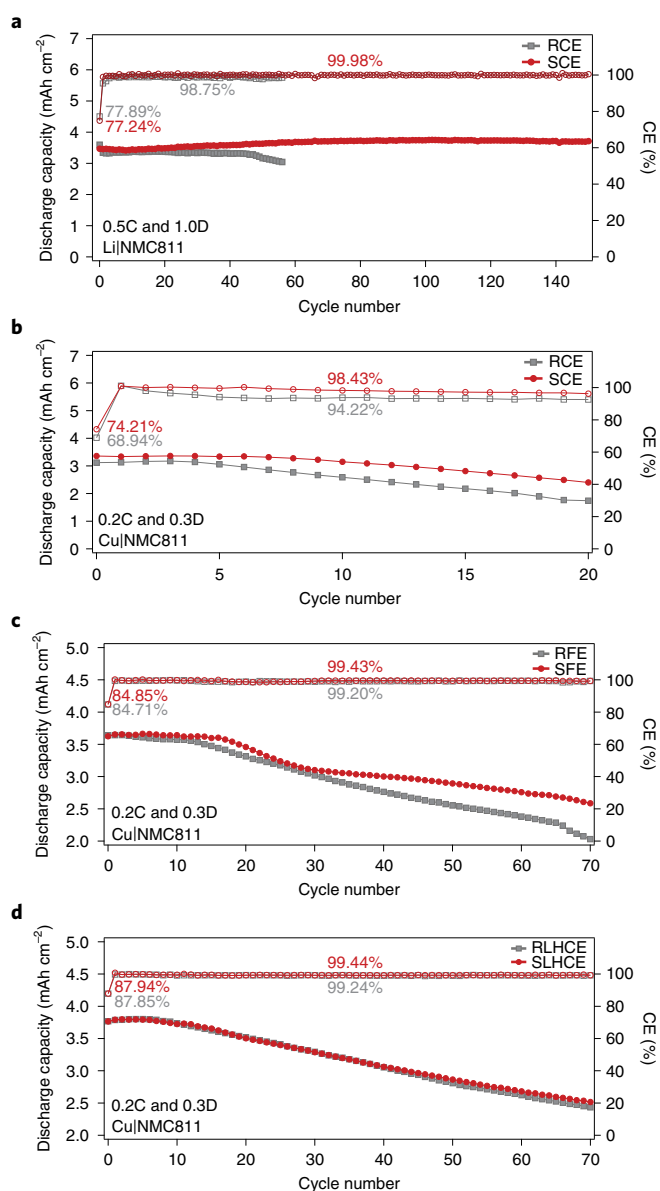


Fig. 6 | Full cell electrochemical performances of the suspension electrolytes. **a**, Representative Li|NMC811 full cell cycling profiles of the discharge capacity (filled symbols) and CE (open symbols) with RCE and SCE. The cycling was performed at 0.5C and 1.0D, where the C and D represent charging and discharging C rates, with the voltage window of 3.0–4.3 V versus Li/Li⁺. The first cycle CE and the CE averaged over the rest of the cycle are displayed for RCE and SCE. **b**, Representative anode-free Cu|NMC811 cell cycling profiles of the discharge capacity (filled symbols) and CE (open symbols) with RCE and SCE. The cycling was performed at 0.2C and 0.3D with the voltage window of 3.0–4.3 V versus Li/Li⁺. The first cycle CE and CE averaged over the rest of the cycle are displayed for RCE and SCE. **c**, Representative anode-free Cu|NMC811 cell cycling profiles of the discharge capacity (filled symbols) and CE (open symbols) with RFE and SFE. The cycling was performed at 0.2C and 0.3D with the voltage window of 3.0–4.3 V versus Li/Li⁺. The first cycle CE and CE averaged over the rest of the cycle are displayed for RFE and SFE. **d**, Representative anode-free Cu|NMC811 cell cycling profiles of the discharge capacity (filled symbols) and CE (open symbols) with RLHCE and SLHCE. The cycling was performed at 0.2C and 0.3D with the voltage window of 3.0–4.3 V versus Li/Li⁺. The first cycle CE and CE averaged over the rest of the cycle are displayed for RLHCE and SLHCE.

overpotential. As evidenced in Supplementary Fig. 21, denser and bulkier Li⁰ electrodeposits were shown for SFE than for RFE. Equivalently, the Li⁰ electrodeposits with SLHCE were also bulkier and more compact than with RLHCE (Supplementary Fig. 22).

The ⁷Li NMR spectra were examined to observe the Li⁺ solvation environment of SLHCE, RLHCE, SFE, RFE, SCE and RCE (Fig. 5c). The peak positions for the high-performance electrolytes (SLHCE, RLHCE, SFE and RFE) were in the upfield region, meaning the solvated Li⁺ in the high-performance electrolytes has a higher electron density than in SCE and RCE. It has been reported that the Li⁺ solvation shells of the high-performance electrolytes contain a relatively large amount of contact ion pairs and ionic aggregates^{5,15,21}. Therefore, the peaks for the high-performance electrolytes were expected to be in the upfield region relative to RCE and SCE. The relative peak shifts based on SCE (4.99%), SFE (1.82%) and SLHCE (1.26%) are summarized in Fig. 5d. It was observed that the relative peak shift was the greatest for SCE and the least for SLHCE; the trends observed in CI_{avg} decrease percentages (Supplementary Fig. 20) agree with the ⁷Li NMR analyses (Fig. 5d). This implies that the effect of the suspension may vary with the choice of electrolyte. Another apparent effect of the suspension is that all the suspension electrolytes exhibited the peak shifts in the upfield direction, suggesting that the suspension in the high-performance electrolytes has similar effects to those observed in SCE. To further clarify this point, XPS analyses were performed with high-performance electrolytes, which showed higher inorganic surface features of SLHCE-iSEI and SFE-iSEI than with RLHCE-iSEI and RFE-iSEI (Supplementary Note 17 with Supplementary Figs. 23–26).

The interfacial impedances of Li⁰ with the high-performance electrolytes were measured to analyse the electrochemical effect of the Li₂O suspension in the high-performance electrolytes (Fig. 5e, Supplementary Fig. 27 and Supplementary Table 5). Lower interfacial impedances of Li⁰ were achieved with SLHCE and SFE relative to those with RLHCE and RFE (Fig. 5e). Also, the interfacial impedance changes before and after Li⁰ electrodeposition (Supplementary Figs. 28 and 29) with SLHCE and SFE were smaller than with RLHCE and RFE. Therefore, the interphases that Li⁰ forms with the suspension electrolytes (SCE, SFE and SLHCE) were favourable and electrochemically stable.

Full cell performances with the suspension electrolytes

The suspension electrolytes were paired with a LiNi_{0.8}Mn_{0.1}Co_{0.1} (NMC811) cathode to construct Li|NMC811 and Cu|NMC811 full cells (Fig. 6). Li|NMC811 cells with a large excess of Li⁰ anode and an electrolyte loading of 5 μl mA h_{NMC811}⁻¹ were cycled between 3.0 V and 4.3 V versus Li/Li⁺ with RCE and SCE (Fig. 6a). These parameters were chosen to observe the cell failure restricted by the electrolyte depletion or impedance build-up in the electrode of the cells, which largely depend on the electrolyte performance. Li|NMC811 full cells (Fig. 6a) with SCE at 0.5C (0.5C) and 1.0C (1.0D) rates exhibited prolonged cycle life compared to that of RCE. This improvement signifies that the electrolyte consumption and/or the rate of undesired interfacial impedance build-up during the cycling were relatively reduced with SCE. Although the theoretical oxidation potential of Li₂O (3.1 V versus Li/Li⁺)⁴² is lower than the operating potential of NMC811 (3.0–4.3 V versus Li/Li⁺), the suspension electrolyte design enabled the stable cycling of the Li₂O suspension in the full cell up to 4.5 V versus Li/Li⁺ (Supplementary Note 18 with Supplementary Figs. 30 and 31). Also, the cycling characteristics of the suspension electrolyte in the full cell exhibited a weak dependency on gravity, cell orientations and suspension blocking the pores of the separator (Supplementary Note 19 with Supplementary Figs. 31 and 32).

With the specific aim of verifying our suspension electrolyte design under more realistic conditions for practical LMBs, we explored the cycling performance of the suspension electrolytes in

the anode-free (Cu|NMC811) cell configuration with a lean electrolyte loading of $2.5 \mu\text{mAh}_{\text{NMC811}}^{-1}$. The cycling performance of Cu|NMC811 with SCE at 0.2C and 0.3D exhibited a 5.27% higher first cycle CE and 4.21% higher cycling CE from the second to the 20th cycle with improved capacity retentions, compared with that of RCE (Fig. 6b). The cycling voltage profiles of RCE and SCE (Supplementary Fig. 33) indicate that active Li^0 was stably utilized over the cycles, as cycling voltage profiles of the cell with SCE showed a constant slope of charging voltage curves and constant-voltage charging profile length^{43,44}, whereas increased voltage-curve slopes and lengthened constant-voltage profiles were shown with RCE. The cycling profiles of the anode-free cells with RFE and SFE at 0.2C and 0.3D are shown in Fig. 6c, where improved CE and capacity retentions were obtained with SFE. In a similar manner, stabilized charge/discharge voltage profiles were also achieved with SFE (Supplementary Fig. 34). Interestingly, although improved overall CEs of SLHCE were observed (Fig. 6d and Supplementary Fig. 35), the degree of the performance improvement was not as much as in SCE and SFE. This could be realized from the least peak shift observed in ^7Li NMR (Fig. 5d) and Cl_{avg} decrease (Supplementary Fig. 20), in which the impact of the suspension in the Li^+ solvation change and CE improvement was least for SLHCE. The full cell cycling profiles with multiple cells are shown in Supplementary Fig. 36. Moreover, detailed explanations are provided in Supplementary Note 20 to correlate the mechanism of the suspension electrolyte to the electrochemical performance improvement of the Li^0 anode. The possible factors that may affect the suspension electrolytes and future insights are discussed in Supplementary Note 21 with Supplementary Fig. 37.

Conclusions

In this work, we present a suspension electrolyte design to derive favourable SEIs on Li^0 for LMBs. Li_2O -based suspension electrolytes were investigated in detail as proof of concept. We found that the addition of Li_2O into the liquid electrolytes resulted in improved CE, reduced nucleation overpotential, stabilized Li^0 interphase and improved electrochemical performances in full cells. Moreover, the suspension electrolyte design has been extended to state-of-the-art high-performance electrolytes to confirm that the suspension electrolytes are not limited to a particular electrolyte system. Most importantly, we were able to determine essential roles played by Li_2O in the liquid electrolyte employing the suspension electrolyte design. Hence, the suspension electrolyte design potentially serves as a useful study platform to closely observe explicit features of the inorganics that are essential to the SEIs for LMBs. We expect the suspension electrolyte design to evolve into a better understanding of (1) inorganics in SEIs for the Li^0 anode, (2) a facile and universal strategy for designing electrolytes and (3) modifying the Li^+ solvation environment to derive favourable SEIs on the Li^0 anode to develop reliable LMBs.

Online content

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Methods

Materials. All the electrolytes were prepared and made in an Ar-filled glove box with an O₂ concentration below 0.2 ppm and H₂O concentration below 0.01 ppm. The RCE was prepared with 1 M LiPF₆ in EC/DEC (1:1 v/v; Gotion LP 40) with 10 vol% FEC (BASF). The RFE was prepared with 1 M LiFSI (Oakwood) in FDMB. The FDMB was synthesized by following a previous method¹⁵. The RLHCE was prepared with 1 M LiFSI (Oakwood) in TTE (Synquest Laboratories)/DME (Sigma-Aldrich; 0.78:0.22 v/v). Li₂O nanoparticles (~80–100 nm in diameter) were used and purchased from Nanoshel. Li₂O microparticles (100 mesh) were used and purchased from Alfa-Aesar. SCE, SFE and SLHCE were prepared by dispersing 7 wt% Li₂O and about 5.9% volume ratio of Li₂O versus electrolyte (otherwise indicated) into RCE, RFE and RLHCE. All the suspension electrolytes were freshly made by mixing dried Li₂O nanoparticles or microparticles (stored inside of the glove box) with fresh liquid electrolyte right before the measurements. DME, dioxolane (DOL) and DEC were purchased from Sigma-Aldrich to perform the solvation energy measurements. High-purity Li foil (500 µm, 99.9%; Alfa Aesar), Cu foil (Pred Materials), 11 µm polyethylene separator (W-Scope) and NMC811 (Targray) were used to make 2032-type coin cells.

MD simulations. MD simulations were carried out using Gromacs 2018 (ref. ⁴⁵), with electrolyte molar ratios taken from those used in the experimental work. Molecular forces were calculated using the Optimized Potentials for Liquid Simulations all atom (OPLS-AA) force field⁴⁶. Topology files and bonded and Lennard-Jones parameters for carbonates were generated using the LigParGen server⁴⁷, while parameters for PF₆⁻ and Li₂O were taken from the literature^{48,49}. Atomic partial charges for carbonates and PF₆⁻ were calculated by fitting the molecular electrostatic potential at atomic centres in Gaussian16 using the Møller–Plesset second-order perturbation method with a cc-pVTZ basis set. The simulation procedure for the bulk electrolyte (analogous to the RCE) consists of an energy minimization using the steepest descent method followed by a 4 ns equilibration step using a Berendsen barostat and a 20 ns production run using a Parrinello–Rahman barostat, both at a reference pressure of 1 bar. A Nosé–Hoover thermostat was used throughout with a reference temperature of 300 K. The particle mesh Ewald method was used to calculate electrostatic interactions, with a real-space cut-off of 0.12 nm and a Fourier spacing of 0.12 nm. The Verlet cut-off scheme was used to generate pair lists. A cut-off of 0.12 nm was used for non-bonded Lennard-Jones interactions. Periodic boundary conditions were applied in all directions. Bonds with hydrogen atoms were constrained. Convergence of the system energy, temperature and box size were checked to verify equilibration. The final 10 ns of the production run were used to generate results.

Simulations were also carried out with a lithium oxide slab to understand the effect of the oxide suspension. The (111) surface was modelled, as it is reported to be the most stable surface⁵⁰. The slab was approximately 1.2 nm thick to ensure screening of any unphysical interactions between liquid electrolytes on either side of the slab. The slabs were observed to be structurally stable over the course of the simulation; however, to ensure accurate simulation of the ordered crystalline structure, positional restraints were also implemented for atoms in the slab with a force constant of 1,000 kJ mol⁻¹ nm⁻². For simulations with the slab, the system was made incompressible in the *x* and *y* directions but allowed to compress in the *z* direction (perpendicular to the slab). A relatively long simulation box was used (approximately 17 nm in the *z* direction after equilibration relative to approximately 5 nm in the *x* and *y* dimensions) to ensure that conditions far from the slab matched those in the RCE simulation. Other details of the simulations with lithium oxide matched those of the RCE simulations except that the equilibration step was lengthened to 10 ns. Simulations conducted without the use of positional restraints yielded similar results.

Density profiles and RDFs were generated using Gromacs, while visualizations were generated with VMD⁵¹. Solvation shell statistics were calculated using the MDAnalysis Python package⁵² by histogramming the observed first solvation shells for lithium ions during the production simulation, using a method similar to previous work¹⁵. A cut-off distance of 0.5 nm from the surface for lithium ions was chosen to evaluate the solvation shells near the surface in order to capture the observed lithium adsorption peak in the density profile near the surface. The solvent shell calculations for ‘near’ the surface were defined as the shell of any lithium ion within 0.5 nm of the surface. Therefore, some solvent or counterions farther from the surface would have been counted, but the lithium ions were within 0.5 nm. The cut-off for each species in the first Li solvation shell was calculated from the first minimum occurring in the RDF (referenced to lithium ions) after the initial peak.

DFT simulations. The calculations were performed with the DFT code GPAW^{53–55}. The Perdew–Burke–Ernzerhof⁵⁶ functional within the generalized gradient approximation was used to describe the electron exchange–correlation effect. Plane-wave basis sets and the projector augmented-wave method were used for electronic wavefunctions. The energy cut-off of 450 eV was applied to all the calculations. The *k*-point grid of 2 × 2 × 1 was used for Li₂O slab calculations. The energy and forces per atom were converged to within 10⁻⁴ eV and 10⁻³ eV Å⁻¹, respectively. For the slab calculations, the vacuum thickness was chosen to be 15 Å to reduce artificial interactions due to periodic boundary conditions. The Li₂O

slab consisted of six layers of unit cells (spanning approximately 15 Å) in the *z* direction. For Li adsorption calculations, atoms below the top four atomic layers were constrained during geometry optimization.

Characterizations. *Cryo-STEM and SEM.* For TEM sample preparation, Cu TEM grids were used as the working electrode for Li metal plating. A total capacity of 0.1 mAh cm⁻² was deposited under a constant current of 1 mA cm⁻². The Li/Cu TEM grid coin cells were disassembled in an argon-filled glove box. TEM grids were rinsed with 60 µl of pure DEC to remove residual salts and dried before freezing. Then, the TEM grid was sealed in an airtight container, which was immediately submerged and crushed in liquid nitrogen to rapidly expose the sample to cryogen without air exposure.

For cryo-STEM characterization, while immersed in liquid nitrogen, the sample was loaded into the Gatan side-entry cryo-transfer holder (Gatan model 626) and inserted into the TEM column. The cryo-STEM/TEM holder uses a specialized cryo-shutter to prevent air exposure and ice condensation onto the sample. Once inside the TEM column, the temperature was maintained at approximately –178 °C.

Cryo-STEM experiments were performed on a ThermoFisher Titan 80–300 environmental (scanning) transmission electron microscope operated at an accelerating voltage of 300 kV. The instrument is equipped with an aberration corrector in the image-forming lens, which was tuned before each sample analysis. Cryo-TEM images were acquired by a Gatan K3 IS direct-detection camera in electron-counting mode. Cryo-STEM/TEM images were taken with an electron dose rate of around 100 e⁻ Å⁻² s⁻¹, and a total of five frames were taken with 0.1 s per frame for each image.

Cryo-STEM EELS characterization was performed with a C2 aperture of 50 nm, a probe current of 75 pA, a camera length of 38 mm and a pixel dwell time of 100 ms. EELS spectra were acquired on a high-resolution Gatan imaging filter (GIF Quantum 966) with a dispersion of 0.25 eV per channel in dual EELS mode. Maps were computed through a two-window method, with a pre-edge window fitted to a power-law background and a post-edge window of 20–40 eV on the core-loss signal.

Solvation energy measurements. Please refer to the literature³⁹ for the detailed apparatus set-up. In brief, 1 M LiFSI in DEC and 3 M LiFSI in DME/DOL were used for EL_{ref} and the salt bridge, respectively. RCE, 20 wt% Li₂O nanoparticles in SCE, and 20 wt% Li₂O microparticles in RCE were used for EL_{test}. The cell potentials were measured by Biologic VMP3 using the H-cell (EL_{ref}|salt-bridge|EL_{test}) with Li electrodes in contact with EL_{ref} and EL_{test}. The cell potentials were measured for each of the EL_{test}; the cell potentials and solvation energies were recorded for 3 seconds; and averaged values were reported.

The ⁷Li NMR spectroscopy. A capillary tube insert sealed with a polytetrafluoroethylene cap was used for NMR experiments. The outer tube contained freshly prepared suspension electrolyte and the inner tube contained 1 M LiCl in D₂O as an external reference. The ⁷Li NMR was performed on a Varian Inova 500 MHz NMR instrument. The external reference was used for locking and shimming. The chemical shifts were referenced to 1 M LiCl in D₂O at 0 ppm.

XPS. The characterization was performed on a PHI Versaprobe I with a monochromatized Al Kα X-ray source. The chamber was kept at a pressure of about 10⁻⁷ Pa during characterization. High-purity Li foil (750 µm, 99.9%; Alfa Aesar) was used. Prior to characterization, the Li surface was rinsed with 60 µl of pure solvent (DEC for carbonate-based electrolytes and DME for ether-based electrolytes) in an Ar-filled glove box to remove residual salt. A vacuum transfer vessel was used to transfer the samples directly from the Ar glove box to the vacuum transfer chamber of the instrument to prevent air exposure. High-resolution spectra were calibrated using the C 1s peak at 284.6 eV.

Electrochemical measurements. Three reference (RCE, RFE and RLHCE) and three suspension (SCE, SFE and SLHCE) electrolytes were used in this study. For Li|Cu, Li|Li and Li|NMC811 cells, 20 µl of the specified electrolytes were used. For Cu|NMC811 cells, 10 µl of the specified electrolytes were used. Electrochemical impedance spectroscopy was measured by Biologics VMP3 with the frequency ranging from 7 MHz to 100 mHz. Cyclic voltammetry was measured by Biologics VMP3 with a scan rate of 0.1 mV s⁻¹ and voltage window of 3–4.5 V versus Li/Li⁺ using RCE and SCE in Li|NMC811 cells. Linear sweep voltammetry was measured by Biologics VMP3 with a scan rate of 1 mV s⁻¹ and voltage window of 3–5 V versus Li/Li⁺ using RCE and SCE in Li|Al cells. For Li|Cu, Li|Li and Li|NMC811 cells, the measurements were done by Arbin and Land instruments. For CE and nucleation overpotential measurements from Li|Cu cells, a current density of 0.05 mA cm⁻² was used with a cut-off voltage of 1 V versus Li/Li⁺ to cycle. For Li|NMC811 and Cu|NMC811 cells, specified charging and discharging C rates were used with the voltage window of 3.0–4.3 V versus Li/Li⁺, where the constant current goes up to 4.2 V versus Li/Li⁺ and the constant voltage was held at 4.3 V versus Li/Li⁺, with the cut-off current value of 0.05 C. Galvanostatic charging up to 4.2 V versus Li/Li⁺ was considered to closely observe the performance impact of the Li⁰ anode in the full cells over the cycles as the NMC811 cathode runs relatively stably between 3 V

and 4.2 V versus Li/Li⁺. In this way, it becomes easier to decouple the impact of the electrochemical performance between the Li⁰ anode and NMC811 cathode. The constant-voltage charging at 4.3 V versus Li/Li⁺ was considered to extract more capacity from the cathode as the NMC811 cathode exhibits a higher capacity by charging up to 4.3 V than up to 4.2 V versus Li/Li⁺.

Elemental analysis. The electrochemical framework of the Li|NMC811 cell was established based on the theory developed by Newman et al. The ion (including cations and anions) flux in the electrolyte constitutes the electric field between two electrodes, which alters the movement of suspension particles by the dielectrophoretic force

$$\mathbf{F}_E = \frac{\pi}{4} \left(\frac{\epsilon_p - 1}{\epsilon_p + 2} \right) \epsilon_p d_p^3 \text{grad } \mathbf{E}^2$$

where \mathbf{F}_E is the dielectrophoretic force acting on the particles, ϵ_p is the dielectric constant of particles, d_p is the particle diameter and \mathbf{E} is the electric field. Since the particle size is in the nanoscale, the Brownian force also affects to the particle movement:

$$\mathbf{F}_B = \bar{\mathbf{I}} \sqrt{\frac{6\pi k_B \mu T d_p}{\Delta t}}$$

where \mathbf{F}_B is the Brownian force acting on the particles, $\bar{\mathbf{I}}$ is the random directional unit vector, k_B is the Boltzmann's constant, T is the electrolyte temperature, μ is the electrolyte viscosity and Δt is the size of the time step taken by the solver. All the numerical simulation was performed using commercial software COMSOL Multiphysics. The geometrical and electrochemical parameters in the numerical model are set to be consistent with the experimental set-up.

Data availability

The authors declare that all the data and relevant information are available within the article and Supplementary Information. Additional data are available from the corresponding author upon reasonable request.

Code availability

The MD and DFT simulation codes are available at https://github.com/prudnick94/LiSolvation_Li2OSuspension and <https://github.com/exenGT/Li2O>, respectively.

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Author contributions

M.S.K. and Y. Cui conceived the idea and conceptualized the work. M.S.K. performed the experiments and analysed the data with guidance from Y. Cui. M.S.K., Z.Z. and Y. Cui wrote the manuscript. Z.Z. performed cryo-STEM and SEM experiments and analyses. P.E.R. performed MD simulations and analysed the data. J.W. conducted DFT calculations. Z.Y. synthesized FDMB electrolyte and helped to take impedance measurements. S.T.O. performed XPS analysis. Y. Chen performed ⁷Li NMR analysis. S.C.K. measured the cell potential and relative Li⁺ solvation energy of the electrolytes. W.Z. helped take SEM images. Z.Y., H.W., S.C.K., D.T.B., X.K., Z.H. and W.H. provided technical help and helpful discussions. S.F.B. and L.-W.W. reviewed the manuscript. Y. Cui, Z.B. and J.Q. supervised the overall study. All the authors discussed the manuscript and provided comments.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to Yi Cui.

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