

Electrolyte additive enabled fast charging and stable cycling lithium metal batteries

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Batteries using lithium (Li) metal as anodes are considered promising energy storage systems because of their high energy densities. However, safety concerns associated with dendrite growth along with limited cycle life, especially at high charge current densities, hinder their practical uses. Here we report that an optimal amount (0.05 M) of LiPF₆ as an additive in LiTFSI–LiBOB dual-salt/carbonate-solvent-based electrolytes significantly enhances the charging capability and cycling stability of Li metal batteries. In a Li metal battery using a 4-V Li-ion cathode at a moderately high loading of 1.75 mAh cm⁻², a cyclability of 97.1% capacity retention after 500 cycles along with very limited increase in electrode overpotential is accomplished at a charge/discharge current density up to 1.75 mA cm⁻². The fast charging and stable cycling performances are ascribed to the generation of a robust and conductive solid electrolyte interphase at the Li metal surface and stabilization of the Al cathode current collector.

Lithium (Li) metal is regarded as the ultimate anode for energy storage systems because of its ultrahigh specific capacity of 3,860 mAh g⁻¹, a very low redox potential (−3.040 V versus standard hydrogen electrode) and a small gravimetric density of 0.534 g cm⁻³. Secondary Li metal batteries (LMBs) have been extensively studied in the past four decades, and received increasing attention recently because of the growing needs for high-energy-density batteries^{1–4}. However, technical challenges such as unsatisfied coulombic efficiency and dendritic Li growth impede the successful deployment of secondary LMBs. Recently, extensive work has been dedicated to Li metal protection, including the application of polymer or solid-state electrolytes^{5–7}, ionic liquids^{8–10}, concentrated electrolytes or additives,^{11,12} protective layers,^{13,14} interlayers between Li and separator^{15,16}, nanoscale design¹⁷, selective deposition³, Li/reduced graphene oxide composites⁴, and others.

Most applications of LMBs demand high-power performance—that is, fast charging and discharging capabilities. Fast discharging at a 2–4 mA cm⁻² current density has been demonstrated to be beneficial for improving the cyclability of LMBs because of the stabilized Li metal anode protected by a transient liquid layer of a highly concentrated Li⁺ ion electrolyte¹⁸. However, fast charging at >0.6 ~ 0.7 mA cm⁻² is detrimental to LMBs using regular LiPF₆/carbonate-solvent electrolytes because the aggravated evolution of dendritic Li along with the serious attack by the electrolyte results in the fast generation of a fairly resistive layer (that is, the solid electrolyte interphase (SEI)) on the Li metal surface, thus dramatically shortening the lifespan of LMBs^{19,20}. Although a limited improvement in the charging rate of LMBs using carbonate solvent-based electrolytes has been achieved by using a dual-salt electrolyte consisting of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) together with lithium bis(oxalato)borate (LiBOB)²⁰, the stability and the charge rate of these batteries are still far below those required for high-power applications. Therefore, further enhancing the charging

capability and the cycling performance is critically important for enabling successful applications of rechargeable LMBs.

Here we report that significantly improved charging capability and cycling stability of LMBs using a LiNi_{0.4}Mn_{0.4}Co_{0.2}O₂ (NMC, 1.75 mAh cm⁻²) cathode can be achieved via manipulating the lithium salt chemistry in the electrolyte to generate a highly conductive SEI on Li metal. An optimal additive level (0.05 M) of LiPF₆ can greatly alter the interfacial reactions between Li metal and dual-salt electrolyte containing LiTFSI and LiBOB in carbonate solvents. The capacity retention of moderately high areal-capacity Li||NMC batteries could be significantly improved to >97% after 500 cycles at 1.75 mA cm⁻².

Electrochemical properties

The electrochemical properties of Li||NMC batteries using three different electrolytes are presented in Fig. 1. Two formation cycles under about 0.175 mA cm⁻² (C/10 rate) were conducted prior to the subsequent cycling at higher charge/discharge current densities. During the formation cycles, all batteries exhibit almost the same charge/discharge voltage profiles and deliver a similar specific capacity (~160 mAh g⁻¹) that corresponds to a capacity loading of about 1.75 mAh cm⁻² (Supplementary Fig. 1).

Here it is worth mentioning two key parameters—the cathode areal loading and the charge current density—that dictate the capacity fading mechanism of LMBs. A higher cathode loading indicates more utilization of Li in each deposition/stripping process, resulting in more parasitic side reactions, and thus faster capacity fading (Supplementary Fig. 2a). In this work, the deposition and stripping of a large amount of Li (1.75 mAh cm⁻²) in each cycle allow us to reliably evaluate the electrolyte impact on the charging capability of LMBs. On the other hand, a higher charge current density leads to the quicker corrosion of Li metal¹⁹, and therefore leads to faster capacity fading of Li||NMC batteries. Using the conventional

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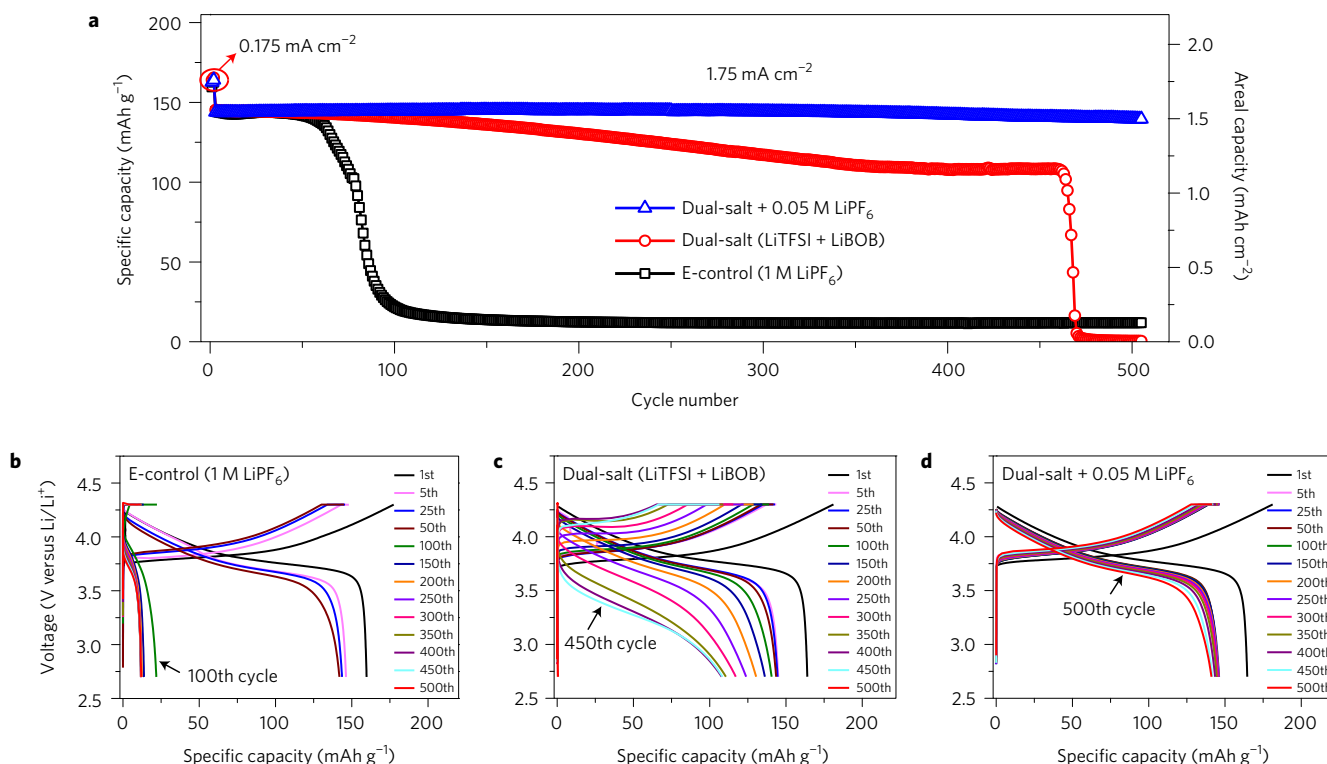


Figure 1 | Electrochemical behaviour of Li||NMC batteries using different carbonate-based electrolytes. **a**, Li||NMC battery cycling performance with various electrolytes in EC-EMC solvent mixture at the same charge and discharge current density of 1.75 mA cm^{-2} after three formation cycles at 0.175 mA cm^{-2} under 30°C . **b–d**, Voltage curves as a function of cycle number of Li||NMC batteries using conventional LiPF_6 electrolyte (**b**), dual-salt (LiTFSI–LiBOB) electrolyte (**c**) and 0.05 M LiPF_6 -added dual-salt electrolyte (**d**).

electrolyte, that is, 1.0 M LiPF_6 in ethylene carbonate (EC) and ethyl methyl carbonate (EMC), the normal operation of the Li||NMC battery is sustained at 0.58 mA cm^{-2} ($\text{C}/3$) for charging, exhibiting a capacity retention of 86.3% at the 500th cycle (Supplementary Fig. 2b). However, with fast charge at 1.75 mA cm^{-2} , the Li||NMC battery experiences an abrupt capacity drop after only about 60 cycles (Fig. 1a). This can be attributed to the quick accumulation of a fairly resistive surface film on the Li metal surface¹⁹. The consequence is a dramatic increase of cell impedance and electrode overpotential (Fig. 1b), leading to battery failure at an early stage.

In comparison, the dual-salt (LiTFSI–LiBOB) electrolyte has better compatibility with Li metal anodes. The corresponding Li||NMC battery shows greatly improved cycle life even at a high charge current density (Fig. 1a). The battery could survive up to 450 cycles prior to sharp capacity drop. However, this battery shows continuous capacity fading and an increased cell overpotential during cycling (Fig. 1c), suggesting the resistive nature of the SEI layer formed in this electrolyte. The capacity retention is only 74.5% after 450 cycles. Surprisingly, with the addition of 0.05 M LiPF_6 as an additive to this dual-salt electrolyte, the Li||NMC battery shows significantly enhanced cycling performance. The battery still retains a high specific capacity of 140 mAh g^{-1} at the 500th cycle at 1.75 mA cm^{-2} , corresponding to 97.1% capacity retention. More importantly, there is only a minimal increase of cell overpotential during 500 cycles (Fig. 1d), indicating that the Li/electrolyte interphase layer is highly conductive for Li^+ ion transportation as compared to those formed in other two electrolytes. To our best knowledge, the performance is the best ever reported for LMBs at such a high charge current density and high positive electrode loading. The fast charging capability of LMBs presented here far exceeds those using concentrated electrolytes and ionic-liquid-based electrolytes^{8,12}.

The electrochemical performance of Li||NMC batteries was also tested at 3.5 mA cm^{-2} (2C rate) and 5.25 mA cm^{-2} (3C rate)

(Supplementary Fig. 3). At these high current densities, significant enhancement in cycle life is again achieved for Li||NMC batteries employing the LiPF_6 -added dual-salt electrolyte. For instance, when cycling at 3.5 mA cm^{-2} , batteries using conventional LiPF_6 solution and the additive-free dual-salt electrolyte reach end of life (EOL, 80% capacity retention) at 55 and 92 cycles, respectively, while the battery using the LiPF_6 -added dual-salt electrolyte can survive more than 200 cycles before the EOL.

In addition, the charging/discharging performance at different C rates was also evaluated, using two different protocols: that is, charge at the constant $\text{C}/5$ rate but discharge at an increasing C rate; and charge at an increasing C rate but discharge with constant $\text{C}/5$ rate. Under different protocols, Li||NMC batteries using the LiPF_6 -added dual-salt electrolyte always show superior charging and discharging capability as compared to the additive-free dual-salt electrolyte and the conventional LiPF_6 electrolyte (Fig. 2).

It is well known that the conventional $\text{LiPF}_6/\text{EC-EMC}$ electrolyte results in a poor SEI layer forming, which contains a large amount of resistive decomposition products of LiF and Li_2CO_3 , as well as other inorganic and organic by-products. Therefore, to reduce the formation of highly resistive LiF , the content of LiPF_6 additive in the dual-salt electrolyte is critical. As presented in Fig. 3a,b, addition of 0.02 M of LiPF_6 is able to considerably enhance the cycle life of Li||NMC batteries at 1.75 mA cm^{-2} . Increasing the amount of LiPF_6 to 0.05 M affords the maximized cycling stability. However, further increase of LiPF_6 content to 0.1 M and 0.2 M leads to degradation of battery performance, showing fast capacity drop at earlier cycles. The reason is that excessive LiPF_6 additive (0.1 M and 0.2 M) actually makes the dual-salt electrolytes behave more like the pure LiPF_6 -based electrolyte—that is, more LiPF_6 will dominate the SEI formation and accelerate the electrolyte consumption, as occurs in the conventional $\text{LiPF}_6/\text{carbonate}$ electrolytes. The optimal LiPF_6 content that is beneficial to dual-salt electrolytes of LiTFSI–LiBOB is $\sim 0.05 \text{ M}$.

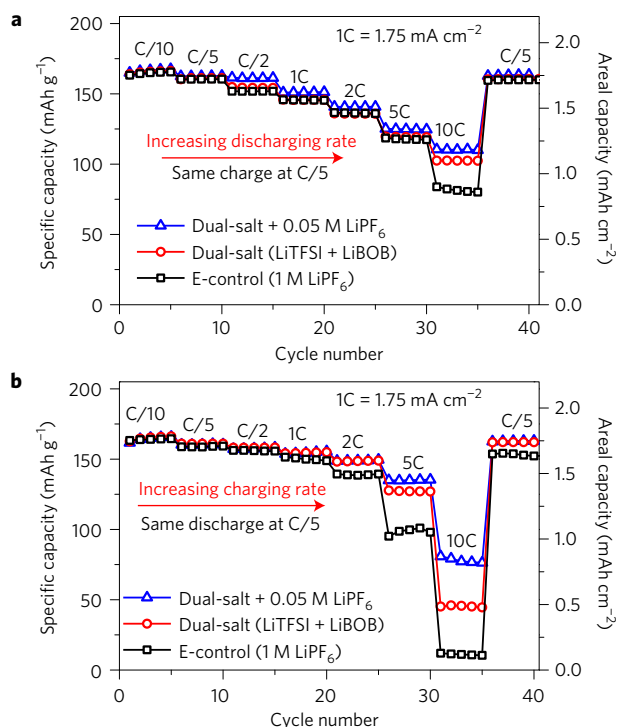


Figure 2 | Rate performance of Li||NMC batteries using various electrolytes at 30 °C. a, Charge at constant C/5 rate but discharge at increasing C rate. **b,** Charge at increasing C rate but discharge at constant C/5 rate. $1C = 1.75 \text{ mA cm}^{-2}$.

The performance of Li||NMC batteries using different electrolytes was further investigated at an elevated temperature (60 °C). Like the 30 °C results, batteries using the conventional LiPF_6 electrolyte as well as the dual-salt electrolyte show inferior cyclability compared to the optimal LiPF_6 -added LiTFSI–LiBOB dual-salt electrolyte (Fig. 3c). An increase in the testing temperature will drastically accelerate the parasitic reactions of Li metal with electrolyte. This will cause the formation of more components in the SEI film and accelerate the degeneration of Li metal, which in turn results in fast capacity loss. Therefore, Li||NMC batteries show a shortened cycle life at 60 °C, regardless of the electrolyte used (Fig. 3c). The batteries using the conventional LiPF_6 electrolyte and the additive-free dual-salt electrolyte terminate stable cycling at only 30 and 213 cycles, respectively. However, the battery using the LiPF_6 -added dual-salt electrolyte can still deliver 147 mAh g^{-1} at the 400th cycle at 1.75 mA cm^{-2} , which corresponds to 90.0% of its initial capacity. All of these superior electrochemical performance results demonstrate that the optimal LiPF_6 -added dual-salt electrolyte has better compatibility with Li metal anodes both in fast charging processes and at elevated temperatures.

Additionally, the cycle life of a Li||NMC battery using the 0.05 M LiPF_6 -added dual-salt electrolyte could be further extended when a lower charge current density is used. At room temperature, a very limited capacity fade after 800 cycles (that is, 0.004375% fade per cycle) together with a high cycling efficiency over 99% was achieved for the Li||NMC battery cycled by charging under 0.58 mA cm^{-2} but discharging under 1.75 mA cm^{-2} (Fig. 3d). Benefiting from its excellent stability toward Li metal, the optimal LiPF_6 -added dual-salt electrolyte could be regarded as an appealing electrolyte for practical applications in rechargeable LMBs. Nevertheless, the average coulombic efficiency of Li metal anode itself (~90.6%) is still not satisfactory due to the instability of carbonate solvents towards Li metal (Supplementary Fig. 4), which requires further improvement in future investigations.

Morphology evolution of Li metal anode during cycling

One question that may be raised regarding these excellent performance results is how the additive level of LiPF_6 could greatly enhance the charging capability and the cyclability of LMBs. Structurally, NMC positive electrodes are fairly stable when charged to 4.3 V because of the limited Li^+ ions ($x < 0.6$ in $\text{Li}_{1-x}\text{MO}_2$) utilized in each charge/discharge process. The NMC electrodes exhibit almost unchanged X-ray diffraction (XRD) patterns after cycling in different electrolytes (Supplementary Fig. 5). To further demonstrate the stability of the surface film formed on positive electrodes, cycled NMC electrodes were retrieved (Supplementary Fig. 6a), reassembled into new batteries with fresh Li metal foils using the regular LiPF_6 electrolyte, and cycled again at 1.75 mA cm^{-2} . All the reassembled batteries show an abrupt capacity drop at about 60–70 cycles (Supplementary Fig. 6b), revealing that the SEI layer, if any, formed on NMC electrodes could not produce the decisive role in improving the cycling stability of LMBs at high current densities. The NMC electrode pre-cycled in the LiPF_6 -added LiTFSI–LiBOB electrolyte does not show any advantage in cycle life. The results confirm with confidence that deterioration of the Li metal anode is the most significant consideration dominating the cycling stability of LMBs cycled at high charge current densities.

To obtain more insightful information, a scanning electron microscope (SEM) was used to scrutinize the morphologies of Li metal anodes after cycling, as displayed in Fig. 4a–f. SEM images of a fresh Li metal foil are presented in Supplementary Fig. 7 as a reference. Noticeable differences are evident on the cycled Li metal, depending on various electrolytes used. The $\text{LiPF}_6/\text{EC-EMC}$ electrolyte leads to substantial cracking (Supplementary Fig. 8a,a1,a2) and significant exacerbation of the bulk Li metal anode (Fig. 4a). Although sporadic needle-like dendritic Li is discernible from the Li metal surface (Fig. 4d), the core part of the bulk Li is constructed by loose Li with nano-to-micro particle sizes. This phenomenon indicates that the poor quality of this SEI layer could not shield the bulk Li against electrolyte attack. Consequently, the cell impedance increases quickly during cycling, as confirmed by the electrochemical impedance spectra (EIS) (see Fig. 4g–i). The electrolyte resistance and the interfacial resistance were estimated from the impedance spectra and summarized in Supplementary Table 1. In particular, the obvious increase in electrolyte resistance, as pointed out with a red arrow in Fig. 4i, suggests depletion of the electrolyte components, which affects the transport of Li^+ ions and terminates the operation of LMBs.

In contrast, the Li metal anodes retrieved from the two dual-salt electrolytes exhibit much different morphologies. The major part of the bulk Li metal anode is still well maintained (Fig. 4b,c), exhibiting a corrosion depth of about 30–50 μm . This surface layer sits only loosely on the top of bulk Li; it is susceptible to external pressure and could be easily peeled off from the bulk Li, especially when cycling the Li anode in additive-free dual-salt electrolyte (Fig. 4b). From the top view (Fig. 4e,f), it is found that the original solid Li metal surface has been transformed to fibrous Li with a length ranging from ~10 to several tens μm , and a diameter of about 1 μm . Formation of fibrous Li is dictated by LiBOB²¹, while LiPF_6 and LiTFSI mainly lead to the deposition of short needle-like Li (Supplementary Fig. 9).

For the additive-free dual-salt electrolyte, besides the fibrous Li formation, some nanosized dendritic Li has also been formed after cycling (Fig. 4e), which could increase the parasitic reactions between Li and electrolyte and cause more electrolyte decomposition and by-product formation. The SEI layer generated in the additive-free dual-salt electrolyte is fairly resistive, as indicated by the considerable increase in charge transfer resistance. In contrast, using LiPF_6 -added dual-salt electrolyte, the Li metal anode has only fibrous Li and some SEI layer skins left after Li stripping (Fig. 4f). Formation of fibrous Li is beneficial for enabling the high charging capability because the improved SEI layer as

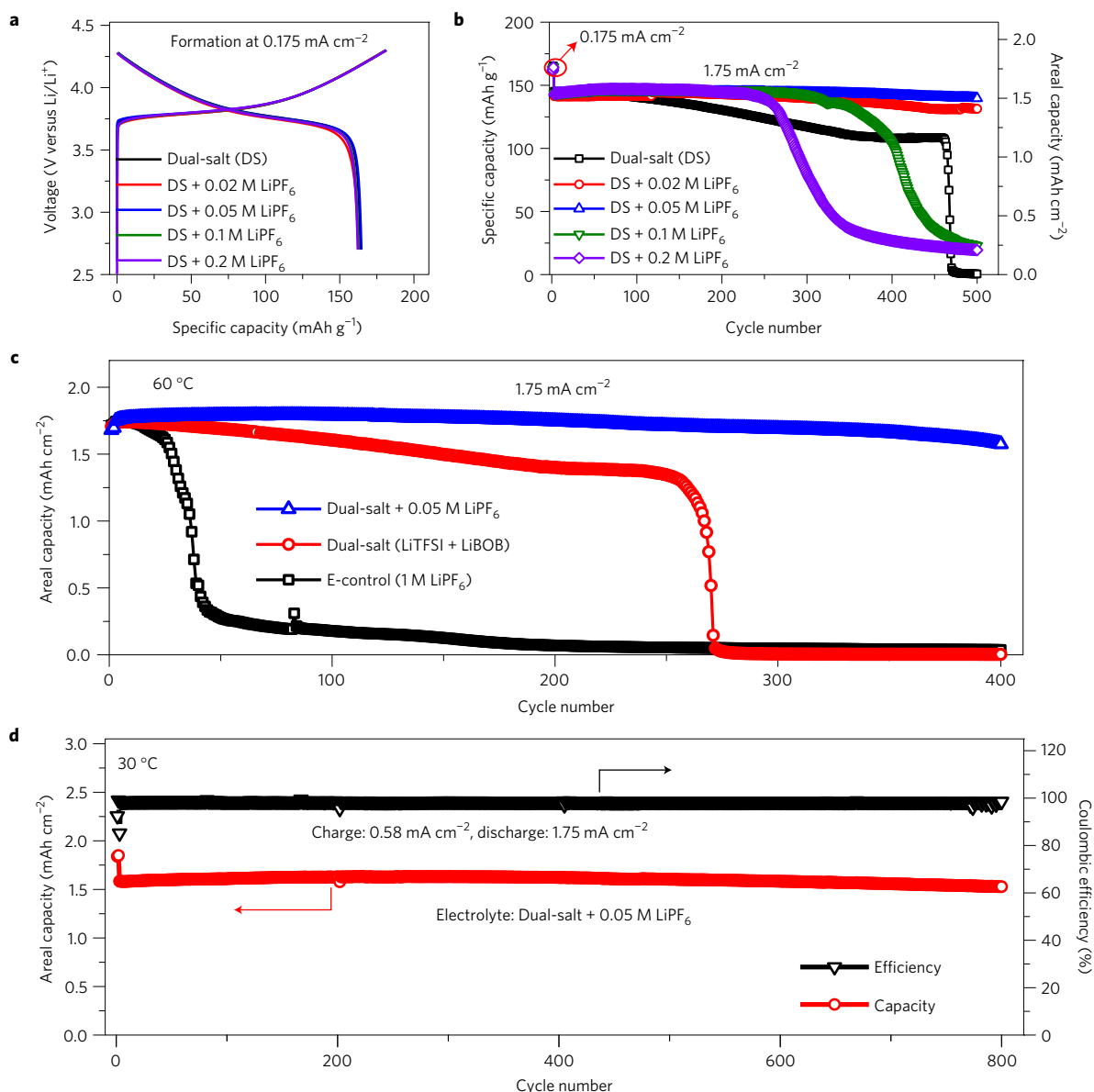


Figure 3 | Effects of additive content and testing conditions. a, b, Initial charge/discharge profiles at 0.175 mA cm⁻² (**a**) and cycling performance (**b**) of Li||NMC batteries with dual-salt electrolytes containing various proportions of LiPF₆ additive at 1.75 mA cm⁻². **c,** Cycling performance of Li||NMC batteries using different electrolytes at a high temperature (60 °C). **d,** Cycling stability of Li||NMC battery using the 0.05 M LiPF₆-added dual-salt electrolyte cycled with 0.58 mA cm⁻² for charge and 1.75 mA cm⁻² for discharge at 30 °C.

modified by the presence of LiPF₆ additive leads to lower charge transfer resistance (Fig. 4h,i). The fast charge transfer nature of the SEI layer formed in the 0.05 M LiPF₆-added dual-salt electrolyte enables the complete stripping of Li that is wrapped by SEI and mitigates accumulation of isolated or 'dead' Li.

SEI layer composition of cycled Li anode

X-ray photoelectron spectroscopy (XPS) was further employed to investigate the components of the SEI layer generated on cycled Li metal. For the Li metal cycled in the LiPF₆-free dual-salt electrolyte, the SEI layer components include the carbonyl group (~289.0 eV (C=O)), polyether carbon (~286.5 eV (CH₂O)), hydrocarbon, (~285.0 eV (CH₂-CH₂O)) in C 1s spectra (Fig. 5a-c), and the carbonyl (~531.0 eV (C=O))/ether oxygen (~533.0 eV (C-O-C)) in O 1s spectra (Fig. 5g-i)^{22,23}. The dominating carbonyl groups could have originated from decompositions of both carbonate solvents and LiBOB salt anions. A significant quantity of Li carbides for example, LiCH₂CH₂OCO₂Li from the reduction of EC, is obviously

observed in this SEI, as indicated by the considerable carbon signal at ~283.0–283.5 eV (refs 22,24). The decomposition products Li₂O, LiF and BO_x could also be confirmed in this SEI layer (Supplementary Fig. 10). The evolution of selected elements with depth profiling is illustrated in Supplementary Fig. 11. An SEI layer like this containing both organic and inorganic segments can hardly prevent Li metal from successive corrosion by the electrolyte. Meanwhile, an SEI layer that was produced in additive-free dual-salt electrolyte seems to be too fragile to protect Li, as evidenced by the earlier exposure of metallic Li after the same time period of XPS sputtering (Supplementary Fig. 10). The depletion of electrolyte and the relatively rapid corrosion of Li metal lead to continuous performance degradation (Figs 1 and 3).

When the electrolyte is replaced with LiPF₆-added dual-salt electrolyte, the Li metal surface is covered with an SEI layer of different components (Fig. 5d-f,j-l). The C 1s spectra show weak peaks with respect to carbides at 283.0–283.5 eV. Alternatively, extra C 1s peaks at 291.0–293.0 eV (Fig. 5d-f) and O 1s peaks

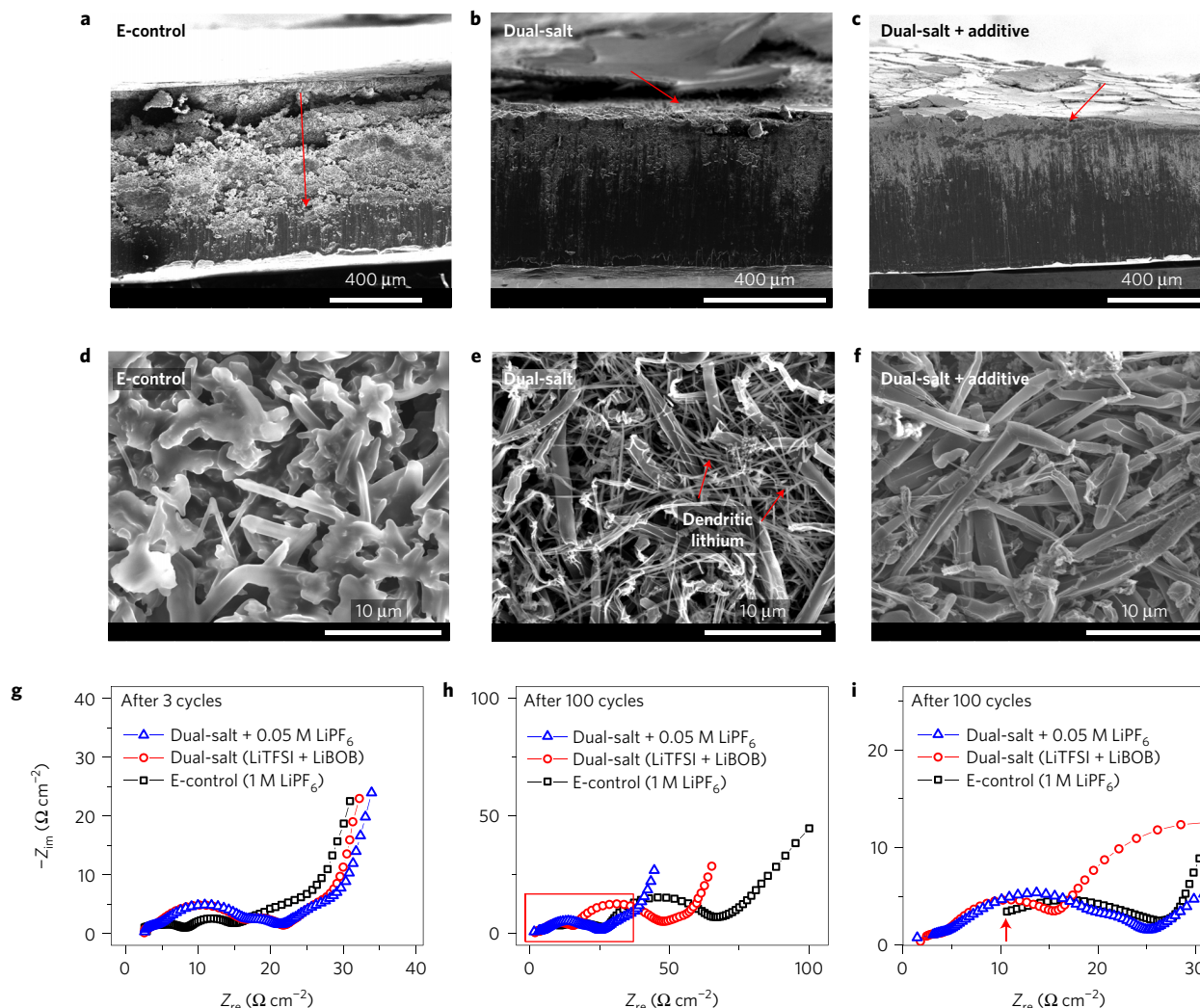


Figure 4 | Morphological and interfacial evolution of Li metal anodes. **a–c**, Cross-section views (**a–c**) and top views (**d–f**) of cycled Li electrodes recovered from Li||NMC batteries following 100 cycles using conventional LiPF_6 electrolyte (**a,d**), dual-salt (LiTFSI-LiBOB) electrolyte (**b,e**) and 0.05 M LiPF_6 -added dual-salt electrolyte (**c,f**). The arrows in **a–c** indicate the different corrosion depth of the Li metal anode. **g–i**, Nyquist plots of Li||NMC batteries using conventional electrolyte, dual-salt electrolyte and 0.05 M LiPF_6 -added dual-salt electrolyte at different stages of cycling. **i**, An enlarged view of the high-frequency region labelled by the red rectangle in **h**.

at 534.0–536.0 eV (Fig. 5j–l) are observed. The result illustrates that the components of the SEI produced in LiPF_6 -added dual-salt electrolyte have higher binding energies than lithium carbonate and lithium alkyl carbonate have^{25,26}, and they could be assigned to polycarbonates [$\text{poly}(\text{CO}_3)$]²². These observations suggest that the LiPF_6 additive helps induce the formation of polycarbonate species, which are more stable to protect Li metal against the electrolyte attack¹⁸. One possibility is that the trace amount of strong Lewis acids PF_5 and POF_3 derived from the additive level of LiPF_6 (through the thermal decomposition of $\text{LiPF}_6 \rightarrow \text{LiF} + \text{PF}_5$, and the hydrolysis of $\text{LiPF}_6 + \text{H}_2\text{O} \rightarrow \text{LiF} + 2\text{HF} + \text{POF}_3$) induces the polymerization of EC solvents. The SEI layer enriched with polycarbonate constituents could effectively mitigate the attack by the electrolyte, and may still permit prompt transport of Li^+ ions and afford sustainable use of LMBs. In addition, the polycarbonate moieties probably have relatively high molecular weights, so they can act in the role of polymer binder to hold other ionically conductive SEI components together and intimately stick to the bulk Li metal anode (Fig. 4c and Supplementary Fig. 8c1,c2).

To gain insight into what functionalities begin to form at higher LiPF_6 additive concentrations, we also performed XPS measurements on the Li metal anodes cycled in 0.1 M and 0.2 M

LiPF_6 -added dual-salt electrolytes (Supplementary Fig. 12). Raising the content of LiPF_6 additive to 0.1 M and 0.2 M in the dual-salt electrolyte not only reduces the formation of $\text{poly}(\text{CO}_3)$ constituents but also increases the formation of inorganic components dominated with carbonates and Li_2O . Such an SEI enriched with inorganic carbonates and Li_2O could not provide enough mechanical strength to maintain the SEI layer from breakdown, so it cannot effectively protect the Li metal against corrosion from the electrolyte. Therefore, higher LiPF_6 additive concentrations again accelerate the consumption of electrolyte, similar to what occurs in the conventional LiPF_6 electrolyte. Therefore, the batteries with 0.1 M and 0.2 M LiPF_6 -added dual-salt electrolytes show fast capacity degradation after a few stable cycles (Fig. 3b).

Electrolyte and SEI layer evolution

Thermodynamically, the electrochemical reduction potential of a lithium salt or solvent is closely related to its lowest unoccupied molecular orbital (LUMO) energy, a lower value of which typically indicates that a chemical is reduced at a higher voltage. The LUMO energy values obtained by molecular dynamics (MD) simulations shown in Fig. 6a demonstrate that the reduction voltage decreases in the following order: $\text{LiBOB} \gg \text{LiTFSI} > \sim \text{LiPF}_6 \gg \text{EC} > \text{EMC}$.

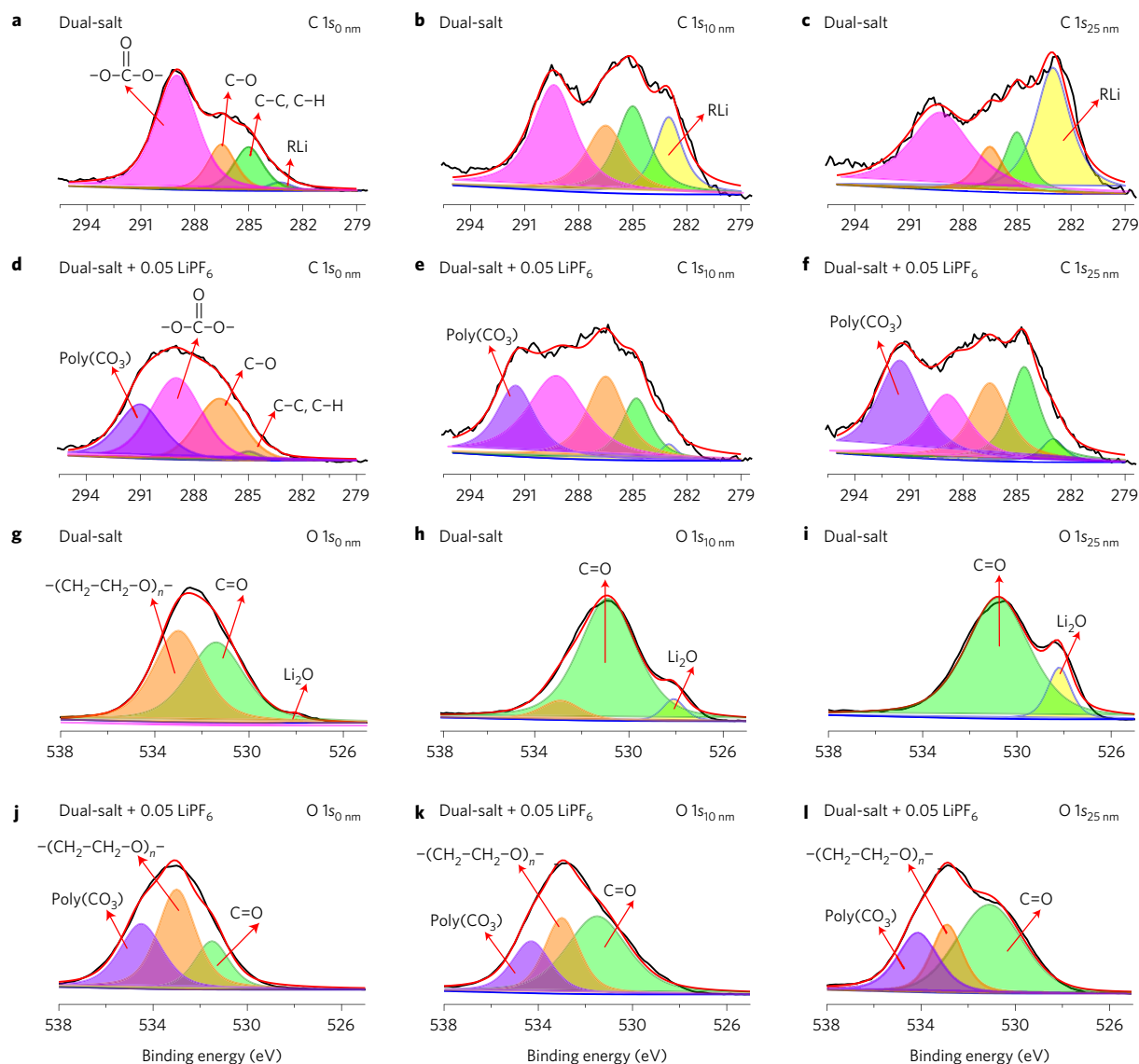


Figure 5 | Characterization of the components of SEI produced on cycled Li metal anodes. a–l, XPS spectra of C 1s (**a–f**) and O 1s (**g–l**) for Li metal retrieved from Li||NMC batteries with dual-salt electrolyte (**a–c, g–i**) or using the LiPF₆-added dual-salt electrolyte (**d–f, j–l**) after two formation cycles under 0.175 mA cm⁻² and ten regular cycles under 1.75 mA cm⁻². C 1s_{0 nm}, C 1s_{10 nm}, C 1s_{25 nm}, and O 1s_{0 nm}, O 1s_{10 nm}, O 1s_{25 nm} indicate the depths at which the C 1s or O 1s spectra were acquired. In the C 1s spectra, the fitted peaks in violet, magenta, orange, olive and yellow are related to polycarbonate, carbonyl group, polyether carbon, hydrocarbon, and lithium carbide species, respectively. In the O 1s spectra, the fitted peaks in violet, orange, olive and yellow are related to polycarbonate, polyether carbon, carbonyl group, and lithium oxides, respectively.

LiBOB could be easily reduced to form an SEI film and hence dictates the morphology of newly deposited Li (Supplementary Fig. 9). Cyclic voltammetry (CV) analysis (Supplementary Fig. 13) is consistent with the LUMO energies, demonstrating that the pure LiBOB shows a reduction peak with an onset voltage at about 1.1 V versus Li/Li⁺, while those for pure LiTFSI and LiPF₆ electrolytes are hard to find. The reduction peak at 1.1 V for LiBOB in the LiTFSI–LiBOB electrolyte is greatly suppressed by the addition of LiPF₆ additive, probably due to the superior SEI layer formed.

The XPS results, as shown in Supplementary Figs. 11 and 12, are also in good accordance with the above LUMO energies. It is surprising to find that the by-products from the decomposition of LiTFSI are in trace amounts, especially the sulfur (S)-containing species, which are hardly detectable in the SEI produced in the dual-salt electrolytes after ten cycles (Supplementary Fig. 10e,f). The LiF found in the SEI generated in the additive-free LiTFSI–LiBOB electrolyte is definitely from the decomposition of LiTFSI (Supplementary Fig. 10a). This may indicate that some of the

S-containing species are soluble in the electrolytes. When LiPF₆ is added, it seems that the decomposition of LiTFSI is suppressed and the Li_xPO_yF_z from the decomposition of LiPF₆ and/or POF₃ is obviously detected (Supplementary Fig. 10b). The evolution of the compositions, or specifically the corresponding elements, in the SEI layers during cycling has been further confirmed with energy dispersive X-ray spectroscopy (EDS) measurements (Fig. 6b,d). After 100 cycles, as compared to B (4.03%) and S (1.08%) found in the SEI layer formed in additive-free dual-salt electrolyte (Fig. 6b), lower contents of B (3.04%) and S (0.22%) elements are detected in the SEI formed in 0.05 M LiPF₆-containing electrolyte (Fig. 6d), suggesting the robustness of the SEI layer and the mitigated reduction of LiTFSI and LiBOB salts in the presence of LiPF₆ additive. The result is consistent with the CV data showing a lower current response and the suppression of the reduction peak of LiBOB during the negative scan (Supplementary Fig. 13f). After 500 cycles in the additive-free LiTFSI–LiBOB electrolyte, the Li surface film has a significant content of Al (Fig. 6c). This was unexpected,

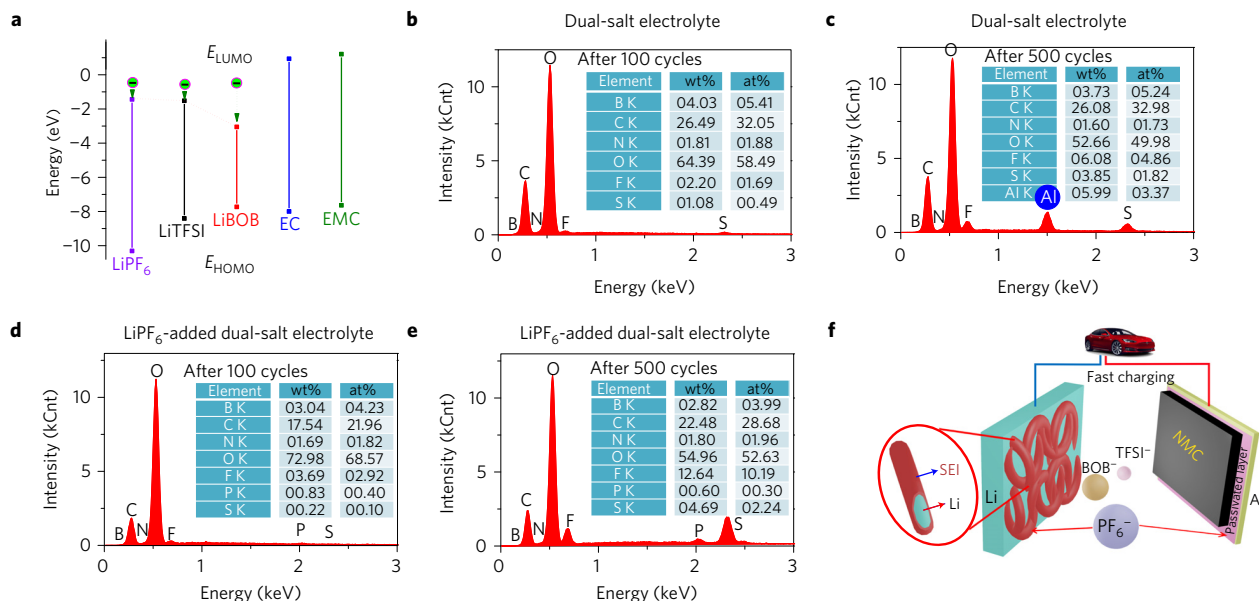


Figure 6 | Molecular orbital energies and evolution of SEI layer compositions. **a**, Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of the lithium salts (LiPF₆, LiTFSI, LiBOB) and solvents (EC, EMC). The vertical lines indicate the electrochemical stability window of related lithium salts and solvents. **b–e**, EDS spectra of Li metal anodes after 100 cycles (**b,d**) and 500 cycles (**c,e**) in the dual-salt electrolytes without (**b,c**) and with (**d,e**) 0.05 M LiPF₆ additive. Insets in **b–e** are the percentages of elements identified in cycled Li metal anodes. **f**, Schematic illustration demonstrating that a LiPF₆ additive in LiTFSI–LiBOB electrolyte prevents the Al corrosion and improves the stability of Li metal.

and indicates that LiTFSI–LiBOB electrolyte without LiPF₆ additive still causes Al corrosion during long-term cycling, and the soluble corrosion product Al(TFSI)₃ diffuses to and deposits onto the Li surface. In contrast, Al corrosion is completely suppressed in the presence of LiPF₆ additive, as reflected by the absence of an Al signal in the EDS spectrum of the Li metal anode after 500 cycles in LiPF₆-added LiTFSI–LiBOB electrolyte (Fig. 6e).

Based on the electrochemical performance and post-mortem analysis, we propose a functioning mechanism of LiPF₆ additive in LiTFSI–LiBOB dual-salt electrolyte (Fig. 6f). On one hand, the LiPF₆ additive is a critical piece in stabilizing Al foil and maintaining electrical connection with the active material. On the other hand, a small amount of LiPF₆ additive greatly alters the nature of the SEI layer generated on the Li anode surface. LiPF₆ additive chemically or electrochemically decomposed to form PF₅, HF and POF₃, which then act as catalysts and induce the formation of polycarbonates from the ring-opening polymerization of EC molecules (Fig. 5d–f,j–l)^{27,28}. The SEI layer produced in the LiPF₆-added dual-salt electrolyte is highly conductive and has very limited effects on the electrode polarization (Fig. 1d and Supplementary Fig. 14), which could prevent the accumulation of isolated/dead Li during each deposition/stripping cycle. In addition, the polycarbonates formed in the SEI layer are flexible, can efficiently cover the Li metal surface, reduce the side reactions, hold the isolated/dead Li particles tightly and adhere to the bulk Li anode, thus preventing the detachment of the SEI layer from the bulk Li metal. Therefore, the utilization of Li metal initiates at the surface and slowly propagates inwards (Fig. 4c). More importantly, there is no internal short circuit occurring with a charge current up to 5.25 mA cm⁻². This high charging capability and the excellent cycle life validate the LiPF₆-added LiTFSI–LiBOB dual-salt electrolyte as an appealing functional electrolyte for high-performance LMBs.

Conclusions

We discovered that an optimal additive amount (0.05 M) of LiPF₆ in the LiTFSI–LiBOB/carbonate electrolytes could greatly enhance the charging performance and the cyclability of LMBs. Stable cycling along with a very limited increase of electrode overpotential

has been achieved at current densities of 1.75 mA cm⁻² and above with the electrode loading of 1.75 mAh cm⁻². The LiPF₆ additive not only plays a critical role in stabilizing the Al current collector, but more importantly also induces the generation of a robust and conductive SEI layer enriched with polycarbonate constituents that can effectively bond the isolated/dead Li with the bulk Li metal anode. The enhanced interfacial stability allows sustainable operation of LMBs at high charge current densities. These key findings offer deep insights to inspire revolutionary improvements in the performance of LMBs through manipulating the salt/solvent/additive chemistry of the electrolytes.

Methods

Materials. Cathode NMC (LiNi_{0.4}Mn_{0.4}Co_{0.2}O₂) electrode laminates (~10.8 mg active material cm⁻²) were supplied by the Cell Analysis, Modelling, and Prototyping (CAMP) Facility located at Argonne National Laboratory (ANL). The electrode laminates were punched into discs and further dried at ~75 °C under vacuum for 12 h. Battery-grade LiPF₆, LiTFSI, EC, and EMC were purchased from BASF. Battery-grade LiBOB was kindly provided by Chemetall for free. These chemicals were kept and handled in a glovebox (MBraun LABmaster) circulated with high-purity Ar gas (<1 ppm O₂ and <1 ppm H₂O). The LiTFSI–LiBOB electrolyte consisting of 0.6 M LiTFSI plus 0.4 M LiBOB in the solvent mixture of EC and EMC (4:6 by wt) was blended inside the glovebox. LiPF₆-added dual-salt electrolytes were prepared through the addition of required amounts of LiPF₆ to the as-prepared dual-salt electrolyte. A control electrolyte (that is, 1.0 M LiPF₆ in the same EC–EMC solvents) was prepared and evaluated for comparison.

Characterization. Structural analysis of NMC electrodes before and after cycling was conducted with a Rigaku MiniFlex II XRD instrument using Cu Kα radiation run at 15 mA and 30 kV. XRD patterns were recorded from 10 ~ 90° in 2θ with a scan speed of 0.1° per min. Morphology observations along with the EDS measurement of cycled Li metal were performed on a Helios focused ion beam SEM at 5.0 kV. For sample preparation, the cycled Li metal samples were soaked in pure EMC for 1 h and then cleaned with pure EMC many times to eliminate remaining electrolytes, and finally dried under vacuum. The cross-sections of Li metal were obtained by using a razor blade to cut the Li metal foils. The XPS testing was carried out using the Physical Electronics Quantera scanning X-ray microprobe, which was outfitted with a monochromatic Al Kα X-ray source (1486.7 eV) for excitation. To avoid side reactions or electrode contamination with ambient oxygen and moisture, Li metal samples were transported from the glovebox to the SEM and XPS instruments in a hermetically sealed container protected by Ar gas.

Electrochemical testing. Charge/discharge performances were measured using CR2032 coin-type batteries. LMBs were constructed using an NMC positive electrode, a foil of Li metal anode, one piece separator (Celgard 2500), and the prepared electrolyte (100 μ l in each battery). Cycling and rate performance tests were carried out with constant current and constant voltage mode using battery testers (Arbin BT-2000). 30 °C or 60 °C environmental chambers were used to keep the temperature stable during the battery performance evaluation. All the Li||NMC batteries were tested between 2.7 and 4.3 V. When the voltage reached 4.3 V, a constant voltage charge process (4.3 V) was applied until the charge current decayed to 0.175 mA cm⁻² (C/10). 1C is equal to 160 mA g⁻¹ or 1.75 mA cm⁻², depending on the active mass loading of NMC cathode material. Current densities of 0.58, 1.75, 3.50 and 5.25 mA cm⁻² were used for cycling performance testing of Li||NMC batteries so as to assess the charging capability of the studied electrolytes. EIS was executed on a 1255B Solartron frequency response analyser coupled with a 1287 potentiostat/galvanostat electrochemical interface (± 10 mV perturbation and $10^5 \sim 10^{-3}$ Hz frequency range).

MD calculations. The highest occupied molecular orbital (HOMO) and LUMO energies of EC, EMC, LiPF₆, LiBOB and LiTFSI were calculated by density functional theory using the Gaussian 09 software²⁹. Geometry optimization simulations were carried out using the basis set of 6-311 + +G(d,p) in conjunction with the functional B3LYP^{30,31}.

Data availability. The supporting data for the included charts/graphs within this paper, as well as other findings from this study, are available from the corresponding author upon reasonable request.

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Author contributions

J.Z., W.X. and J.-G.Z. initiated this research and designed the experiments. B.J.P. prepared and provided the standard NMC electrodes. J.Z. performed the electrochemical measurements with assistance from S.J., as well as the SEM observations. M.H.E. and D.M. performed XPS measurements and molecular dynamics simulations, respectively. J.Z., J.-G.Z., and W.X. prepared this manuscript with input from other co-authors.

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Competing interests

The authors declare no competing financial interests.