Supporting Information

Diffusion Behaviors of Lithium Ions at Cathode/Electrolyte Interface from Global Neural Network Potentials

Yufeng Sun,[a] Cheng Shang,[b] Yi-Bin Fang,[a] Zhi-Pan Liu,[b] Xin-Gao Gong[a] and Ji-Hui Yang*[a]

[a]Key Laboratory for Computational Physical Sciences (MOE), State Key Laboratory of Surface Physics, Department of Physics, Fudan University, Shanghai 200433, China.

[b]Key Laboratory for Computational Physical Sciences (MOE), Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200433, China.

Details of the SSW-NN method for the GNNP training

The SSW-NN method[1,2] which is now incorporated into the Large-scale Atomic Simulation with neural network Potential (LASP) code,[3] is used to produce the GNNP. By reducing the difference between NN and DFT values on total energy, force, and stress, the GNNP is trained using a first-principles density functional theory (DFT) dataset. The SSW global potential energy surface (PES), which includes a large variety of Li_xCoO_2-electrolyte interface, is learned iteratively. the final dataset comprises a total of 25,142 structures, including clusters, bulks, surfaces, and interfaces involving seven elements (Li, Co, O, C, H, P, and F) with the total number of atoms up to 189. To achieve high accuracy for PES, we used a large set of power-type structure descriptors (PTSDs), including 605 descriptors for each element, including 123 2-body, 454 3-body, and 28 4-body descriptors. The network utilized involves three hidden layers (660-80-80-80-4). To normalize the training dataset, min-max scaling is used. Hyperbolic tangent activation functions are used for the hidden layers, and a linear transformation is applied to the output layer of all networks. To match DFT energy, force, and stress, the limited-memory Broyden-Fletcher-Goldfarb-Shanno (L-BFGS) method[4] is used to minimize the loss function.

The comparison between GNNP and AIMD simulations for pure electrolytes

Long-term MD simulations can accurately describe the positional relationship between Li ions and EC/DMC molecules. Therefore, we continue to use the $22.958\,\text{Å} \times 17.040\,\text{Å} \times 19.104\,\text{Å}$ structure composed of 1 mol/L $LiPF_6$ in EC/DMC (1/1 vol%) with a total of 620 atoms. An NVT ensemble simulation is performed at 300 K using our GNNP for 200 ps. The snapshot at 100 ps is also shown in Fig. S1a. Fig. S1b additionally shows the average Li-O RDF within the 102nd ps of the GNNP simulation for 200 ps. It can be found that the number of O atoms in the nearest neighbor decreases compared to that within the 2nd ps.
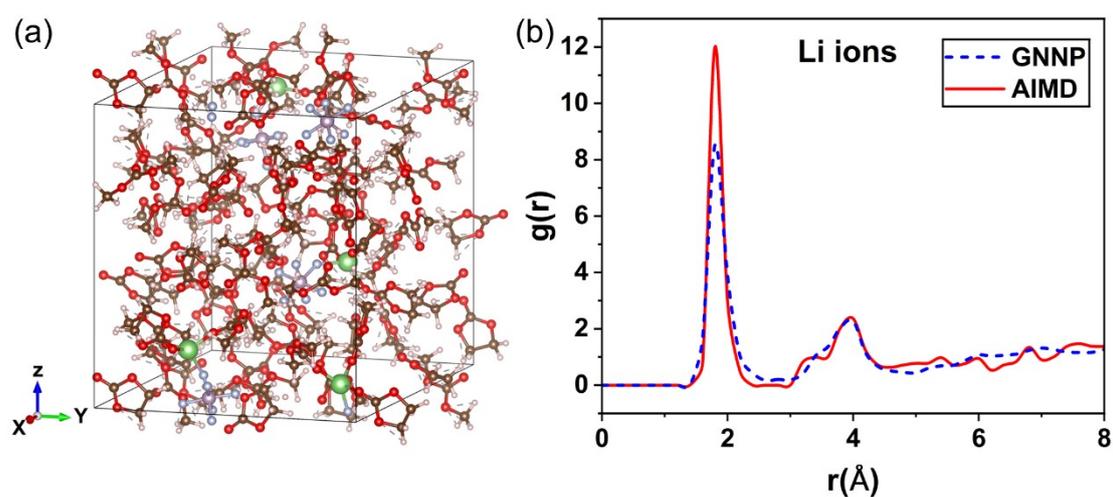
Fig. S1 Comparison of GNNP and AIMD simulations for pure electrolytes. (a) The snapshot structure of pure electrolyte composed of 1 mol/L $LiPF_6$ in EC/DMC (1/1 vol%). (b) Simulated average Li-O RDF for all Li ions in the pure electrolyte. Red are the statistic results within the 2nd ps of the AIMD simulation for 5 ps. Blue dotted lines are the statistic results within the 102nd ps of the GNNP simulation for 200 ps.

The comparison of GNNP simulations for pure electrolytes and cathode/electrolyte interface

Based on the $22.958\,\text{Å} \times 17.040\,\text{Å} \times 50.208\,\text{Å}$ interface structure containing 1912 atoms composed of $LiCoO_2$ ($10\bar{1}4$) and 1 mol/L $LiPF_6$ in EC/DMC (1/1 vol%). We compare the total mean square displacement (MSD) and MSD across the interface (defined as MSD_z) in the solution region of this interface structure with the previously pure electrolyte structure. It also can be found that the formation of the interface results in a decrease in the total MSD, primarily affecting the z-direction diffusion of Li ions in the solution region (Figs. S2a and S2b).
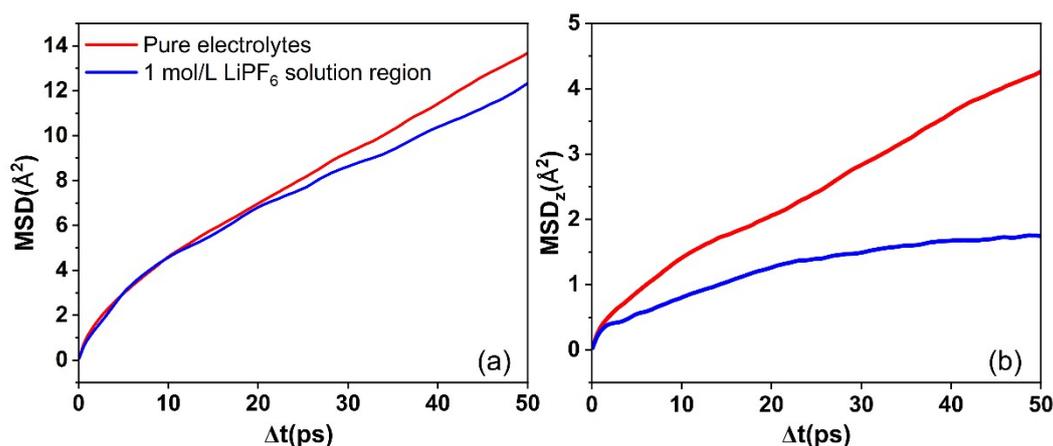
Fig. S2 Comparison of GNNP simulations for pure electrolytes and cathode/electrolyte interface. (a) The total MSD of Li ions in pure electrolytes and in the solution region of LiCoO₂-electrolyte interface. (b) The MSDz of Li ions in pure electrolytes and in the solution region of LiCoO₂-electrolyte interface.

The comparison of the MSD for the first 200 ps and the last 200 ps

Based on the $22.958\ \text{Å} \times 17.040\ \text{Å} \times 50.208\ \text{Å}$ interface structure containing 1912 atoms composed of LiCoO$_2$ ($10\bar{1}4$) and 1 mol/L LiPF$_6$ in EC/DMC (1/1 vol%). The total MSD of Li ions in the solution region obtained using the first 200 ps trajectories are found to be identical to that obtained using the last 200 ps trajectories. Similar conclusions apply for the Li ions in the interface region of this structure (see Figs. S3a and S3b). Consequently, we can conclude that our simulations are already converged within 200 ps. Therefore, for the remaining studies, we just performed 200 ps simulations to save computational costs.
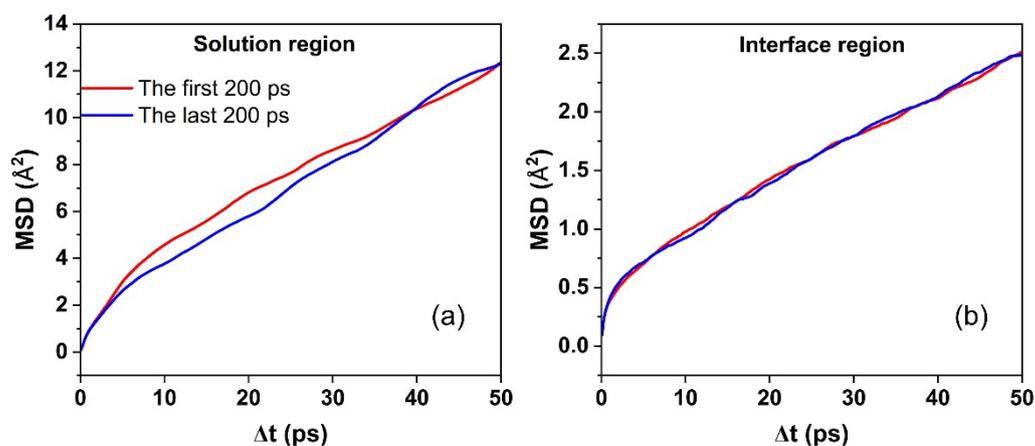

Fig. S3 Comparison of the MSD for the first 200 ps and the last 200 ps. (a) The total MSD of Li ions in the

solution region of the LiCoO₂-electrolyte interface structure for the frist 200 ps and the last 200 ps. (b) The total MSD of Li ions at the interface of the LiCoO₂-electrolyte interface structure for the frist 200 ps and the last 200 ps.

The diffusion coefficient of Li ions at the interface with different electrolyte concentrations

We can obtain the diffusion coefficient (D) of Li ions at the interface with different electrolyte concentrations through this formula:

$$D = \frac{1}{2dt}\langle[r(t)]^2\rangle,$$

where d is the diffusion dimension of Li ions, i.e., d=1 for diffusion across the interface and d=3 for diffusion in the specified three-dimensional region.

The diffusion coefficient of Li ions across the interface remains consistently high and nearly unchanged when the electrolyte concentration is below 1 mol/L. However, it decreases rapidly as the electrolyte concentration continues to increase (Table S1).

Table S1 Calculated diffusion coefficient of Li ions (in unit of cm^2/s) at the interface for cases with different concentrations of LiPF₆.

	0.75 mol/L	1 mol/L	1.25 mol/L	1.5 mol/L
D_s	4.77×10^{-6}	3.17×10^{-6}	2.68×10^{-6}	1.91×10^{-6}
D_i	1.49×10^{-6}	6.34×10^{-7}	6.06×10^{-7}	2.50×10^{-7}
D_{iz}	4.65×10^{-7}	5.86×10^{-7}	2.78×10^{-7}	1.65×10^{-7}

The comparison of the radial distribution function (RDF) for the cathode/electrolyte interface and the interface with the LiF interfacial compound in the solution region

The conductivity of Li ions in the solution region is approximately 25% lower when LiF is present compared to a neat surface. Starting from 100 ps in the NVT ensemble, we calculate the average RDF of Li-O using the trajectories of all Li ions in the solution region based on these interfacial structures. As shown in Fig. S4, on the same timescale as the total MSD analysis, the concentration of F ions in the nearest neighbor shell of Li ions is greater for the interface with the LiF interfacial compound in the solution region compared to that of the cathode/electrolyte interface. This increased presence of F ions near Li ions contributes to a decrease in their
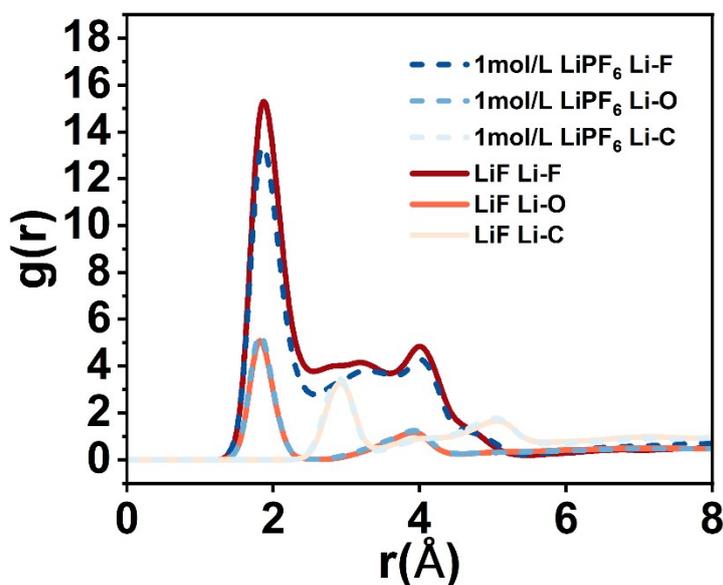
conductivity.

Fig. S4 Comparison of the RDF for the cathode/electrolyte interface and the interface with the LiF interfacial compound. Average Li-F, Li-O and Li-C RDF for all Li ions in the solution region. Red and blue dotted lines are the statistic results of the cathode/electrolyte interface and the interface with the LiF interfacial compound for the same time intervals, respectively.

The comparison of the RDF for the interface with the different interfacial compounds

The different effects of interfacial compounds on the total MSD and MSD_z can be understood by considering the chemical environments around Li ions, which can be reflected by calculating RDF information of Li ions (see Fig. S5). Starting from 100 ps in the NVT ensemble, we calculate the average RDF of Li-Li, Li-O, Li-C and Li-F using the trajectories of all Li ions at the interface based on these interfacial structures. As shown in Figs. S5a-d, on the same timescale as the total MSD analysis, for Li ions, the presence and proximity of other ions or molecules can significantly impact conductivity. In the case of the LiF interface, we observe a clear forward shift in the Li-F RDF peak, attributed to the presence of F ions in LiF. The strong Coulomb interaction between Li and F directly contributes to a decrease in conductivity at the LiF interface. For the Li_2O interface, a small increase in O has a lesser effect compared to the repulsion caused by excess Li ions at the interface. This repulsion leads to a significant increase in conductivity across the interface, even as the overall conductivity decreases. At the Li_2CO_3 interface, an abnormally small peak in the Li-C RDF indicates the influence of C atoms in the carbonate. This suggests a strong binding between

C and Li ions. In general, we find that, if there are more anions such as F^-, O^{2-} and CO_3^{2-} near Li ions and the anion-Li ion distances are shorter, the total MSD will be decreased due to the attractive forces between anions and Li ions. If Li ions have more neighboring Li ions around, the MSD_z will be increased due to the repulsive forces. Moreover, changes in the distances between these nearest-neighbor anions and Li ions have a more significant effect on the behavior of Li ions than small variations in their quantity.
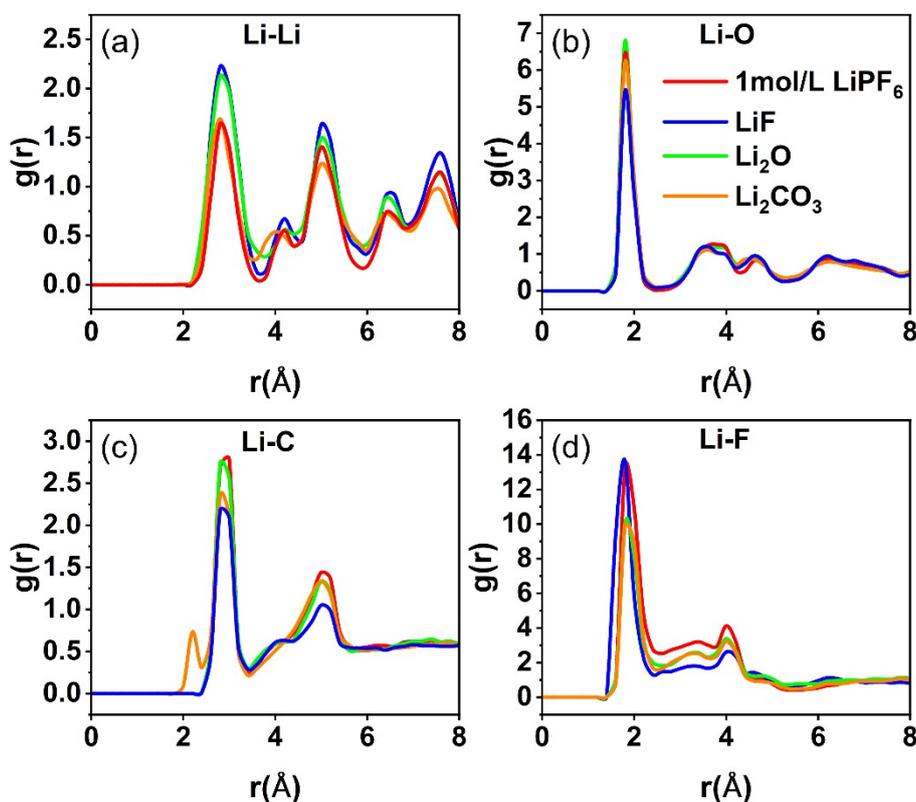

Fig. S5 Comparison of the RDF for the cathode/electrolyte interface and the interface with the LiF, Li₂O, Li₂CO₃ interfacial compound. (a) Average Li-Li RDF for all Li ions at the interface. (b) Average Li-O RDF for all Li ions at the interface. (c) Average Li-C RDF for all Li ions at the interface. (d) Average Li-F RDF for all Li ions at the interface.

The interface structure composed of multiple interfacial compounds and diffusion behavior of Li ions at the interface

The interface structures composed of multiple interfacial compounds are constructed by randomly placing some bulk LiF, Li₂O, and Li₂CO₃ at the interface near the cathode (see Figs. S6a and S6b).

In the bulk LiF, sixteen LiF are included, while the bulk Li_2O contains sixteen Li_2O. For the bulk Li_2CO_3, eight Li_2CO_3 are included. The solution concentration is fixed as 1 mol/L. Similar to the previous simulations, for each structure, we conduct 10 replicas of an initial 50 ps simulation in the NPT ensemble and then a subsequent 200 ps simulation in the NVT ensemble at 300 K. In Fig. S6b, our results show that during the dynamics simulation, distinct diffusion behaviors of Li ions are observed at complex interfaces. Specifically, both active and inactive Li ions coexist at the interface composed of multiple interfacial compounds.
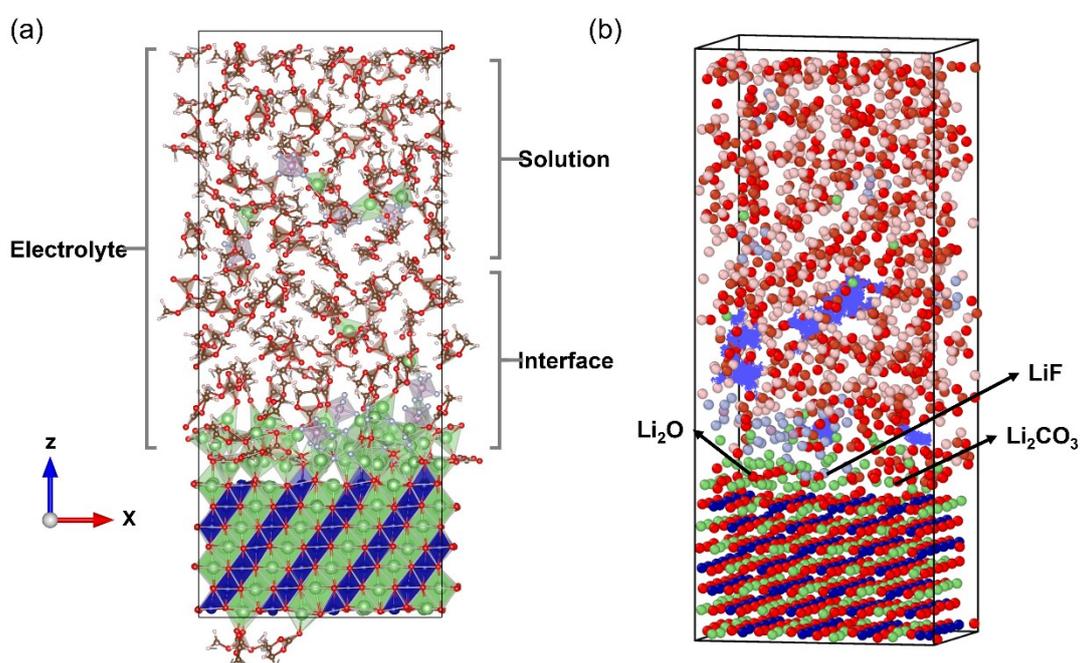

Fig. S6 Diffusion behaviors of Li ions at the interface. (a) The interface structure composed of multiple interfacial compounds, $LiCoO_2$ ($10\bar{1}4$) and 1 mol/L $LiPF_6$ in EC/DMC (1/1 vol%) after relaxation. The system contains sixteen LiF compounds, sixteen Li_2O compounds and eight Li_2CO_3 compounds. The grey brackets show the electrolyte region, the interface region and the solution region which is far from the cathode. (b) Trajectories of Li ions at the interface. The structure shown is the snapshot taken at 200 ps, with the blue lines representing the trajectories of the Li ions over 200 ps.

Then, we study the effects of multiple interfacial compounds including any two of the three compounds: LiF, Li_2O, and Li_2CO_3. The initial structures are constructed by randomly selecting any two of the three bulk materials LiF, Li_2O, and Li_2CO_3, and placing them at the interface near

the cathode, at a distance of 2-3 Å (see Figs. S7a and S7b). The number of LiF, Li$_2$O, and Li$_2$CO$_3$ in the various interface structures are consistent with the interface structure shown in Fig. S6a. The solution concentration is fixed as 1 mol/L. Similar to the previous simulations, for each structure, we conduct 10 replicas of an initial 50 ps simulation in the NPT ensemble and then a subsequent 200 ps simulation in the NVT ensemble at 300 K.

By analyzing the MSD of Li ions (Figs. S7c-S7e) starting from 100 ps, we obtain the following results. For the interface structure formed by multiple interfacial compounds, the MSD of Li ions increases due to the volume effects of multiple interfacial compounds except in the interface containing LiF and Li$_2$CO$_3$. By analyzing the diffusion behavior of Li ions between these interfaces, it reveals that the presence of Li$_2$O is associated with higher Li-ion conductivity across the interface.

As seen in Table S2, we calculate the conductivity of Li ions for interface structures with the presence of multiple interfacial compounds. For the interface with LiF, Li$_2$O and Li$_2$CO$_3$, the conductivity in the solution region increases to 17.66 mS/cm, while the conductivity in the interface region increases to 3.63 mS/cm. In addition, the conductivity across the interface also increases to 3.22 mS/cm. For the interface containing LiF and Li$_2$O, the conductivity in the solution region is 15.05 mS/cm, while the conductivity in the interface region is 4.74 mS/cm, and the conductivity across the interface is 4.41 mS/cm. When examining the interface contained LiF and Li$_2$CO$_3$, the conductivity in the solution region increases to 16.21 mS/cm, while the conductivity in the interface region increases to 2.41 mS/cm but the conductivity across the interface significantly decreases to 1.44 mS/cm. This is also the only structure with multiple interfacial compounds where Li-ion conductivity across the interface decreases. In the case of the interface contained Li$_2$O and Li$_2$CO$_3$, the conductivity in the solution region increases to 22.94 mS/cm, while the conductivity in the interface region increases to 5.90 mS/cm. And the conductivity across the interface also reaches to 5.83 mS/cm. These changes indicate that the presence of Li$_2$O could be a beneficial coating component for the CEI.
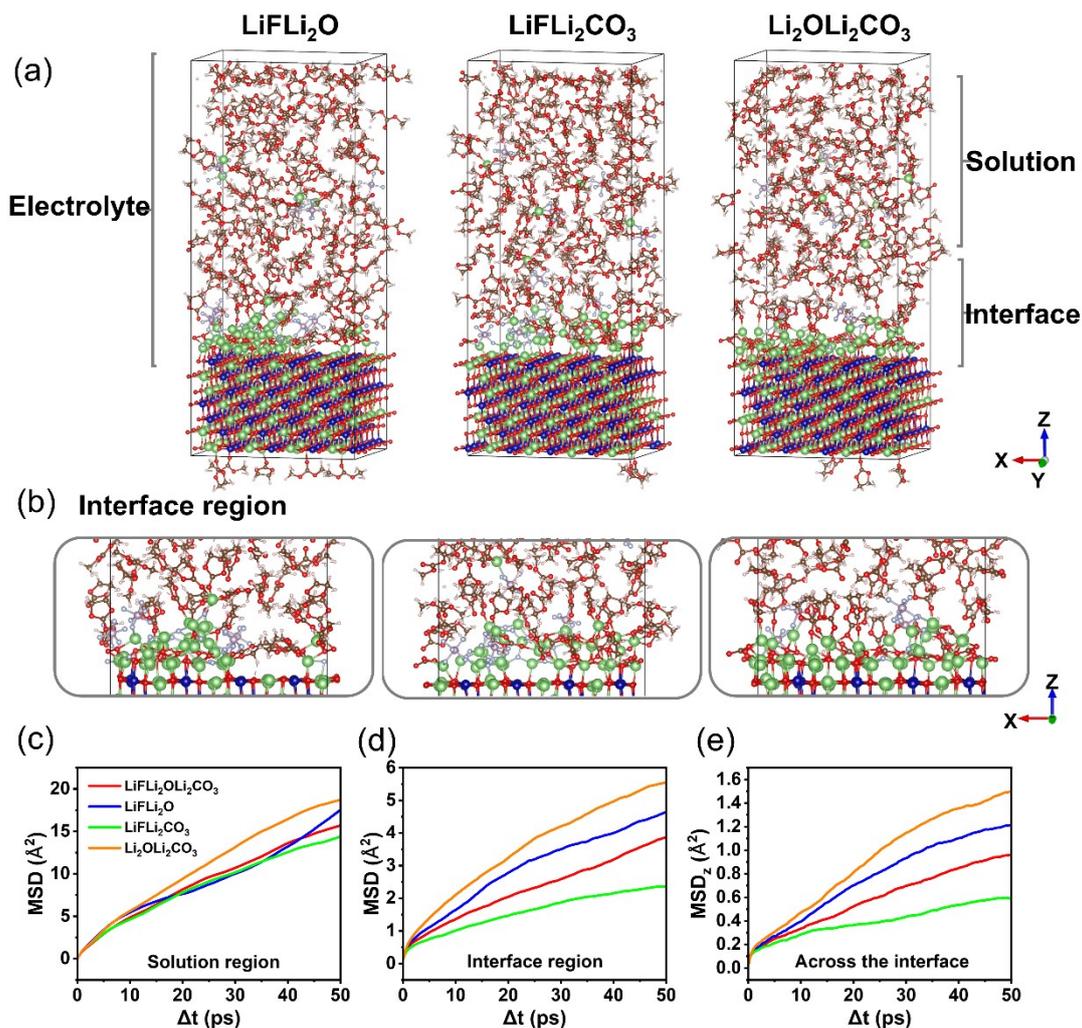
Fig. S7 Interface structures with the presence of multiple interfacial compounds and the corresponding MSD information. (a) The interface structures of the LiCoO$_2$/LiFLi$_2$O-electrolyte interface, the LiCoO$_2$/LiFLi$_2$CO$_3$-electrolyte interface and the LiCoO$_2$/Li$_2$OLi$_2$CO$_3$-electrolyte interface. The LiCoO$_2$/LiFLi$_2$O-electrolyte interface contains sixteen LiF and sixteen Li$_2$O compounds. The LiCoO$_2$/ LiFLi$_2$CO$_3$-electrolyte interface contains sixteen LiF and eight Li$_2$CO$_3$ compounds. The LiCoO$_2$/ Li$_2$OLi$_2$CO$_3$-electrolyte interface contains sixteen Li$_2$O and eight Li$_2$CO$_3$ compounds. (b) The interface regions of the LiCoO$_2$/ LiFLi$_2$O-electrolyte interface, the LiCoO$_2$/ LiFLi$_2$CO$_3$-electrolyte interface and the LiCoO$_2$/ Li$_2$OLi$_2$CO$_3$-electrolyte interface. All the structures are the snapshots at 200 ps. (c) The total MSD of Li ions in the solution region for the cases with different interfacial compounds. (d) The total MSD of Li ions at the interface region for the cases with different interfacial compounds. (e) The MSD$_z$ of Li ions at the interface region for the cases with different interfacial compounds.

Table S2 Calculated conductivities of Li ions (in unit of mS/cm) at the interface for cases with different multiple interfacial compounds.

	$LiFLi_2OLi_2CO_3$	$LiFLi_2O$	$LiFLi_2CO_3$	$Li_2OLi_2CO_3$
σ_s	17.66	15.05	16.21	22.94
σ_i	3.63	4.74	2.41	5.90
σ_{iz}	3.22	4.41	1.44	5.83

References

1 S.-D. Huang, C. Shang, X.-J. Zhang and Z.-P. Liu, *Chem. Sci.*, 2017, **8**, 6327–6337.

2 S.-D. Huang, C. Shang, P.-L. Kang and Z.-P. Liu, *Chem. Sci.*, 2018, **9**, 8644–8655.

3 S. Huang, C. Shang, P. Kang, X. Zhang and Z. Liu, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2019, **9**, e1415.

4 D. R. S. Saputro and P. Widyaningsih, Yogyakarta, Indonesia, 2017, p. 040009.