Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Building a Rigid-Soft Coupling Interphase by Reduction-Oxidation Collaborative Approach with Lithium Difluorobis(oxalato) Phosphate Additive

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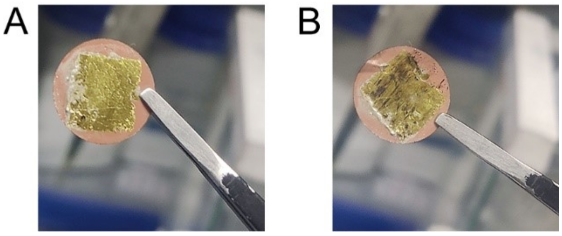

Fig. S1. Pictures of electrodes after discharging in LiDFBOP-added electrolytes: before (A) and after (B) scraping off the surface layer.

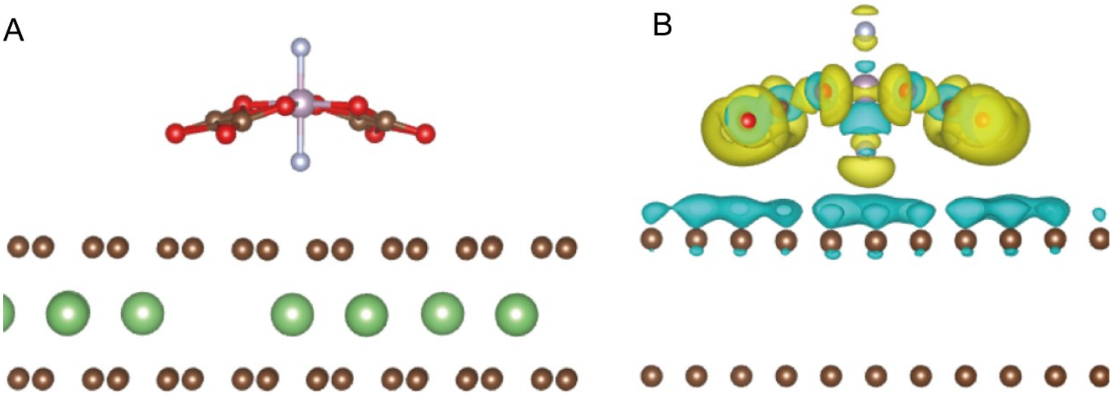

Fig. S2. (A) The molecular structure of an DFBOP$^-$ anion adsorbed on HOPG@Li surfaces (DFBOP@HOPG@Li), and (B) the differential charge density distribution of delithiated DFBOP@LiC$_6$.

Fig. S2 shows the molecular deformation and charge transformation profile of the adsorbed DFBOP$^-$ anions on HOPG@Li surfaces, in which the blue and yellow color represents the accumulation and depletion of charge, respectively. As shown in Fig. S2A, the molecular structure of DFBOP$^-$ anions is changed due to the adsorption effect of HOPG@Li. Furthermore, Fig. S2B illustrates that electrons tend to shift to the HOPG@Li surface. The results suggest that the DFBOP$^-$ anions could be adsorbed on the HOPG@Li surface and lose electrons spontaneously, resulting in the oxidation reaction.

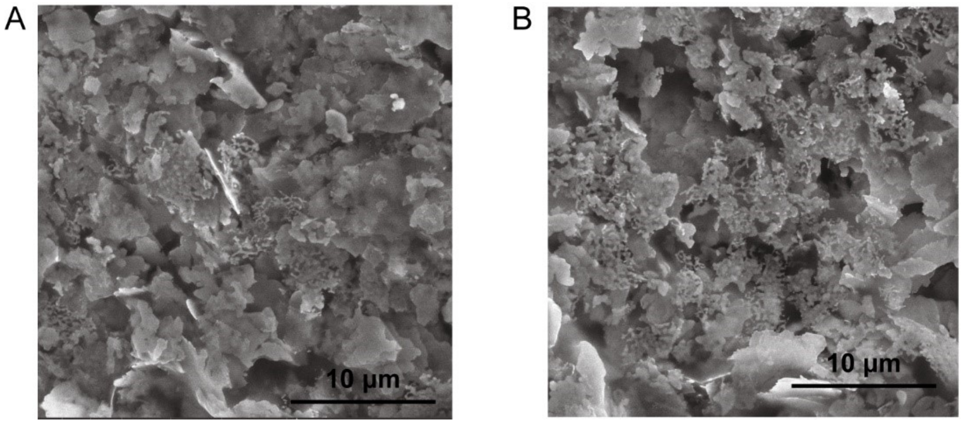

Fig. S3. FESEM images of the reduction and oxidation products of electrolytes that cover the graphite surface.

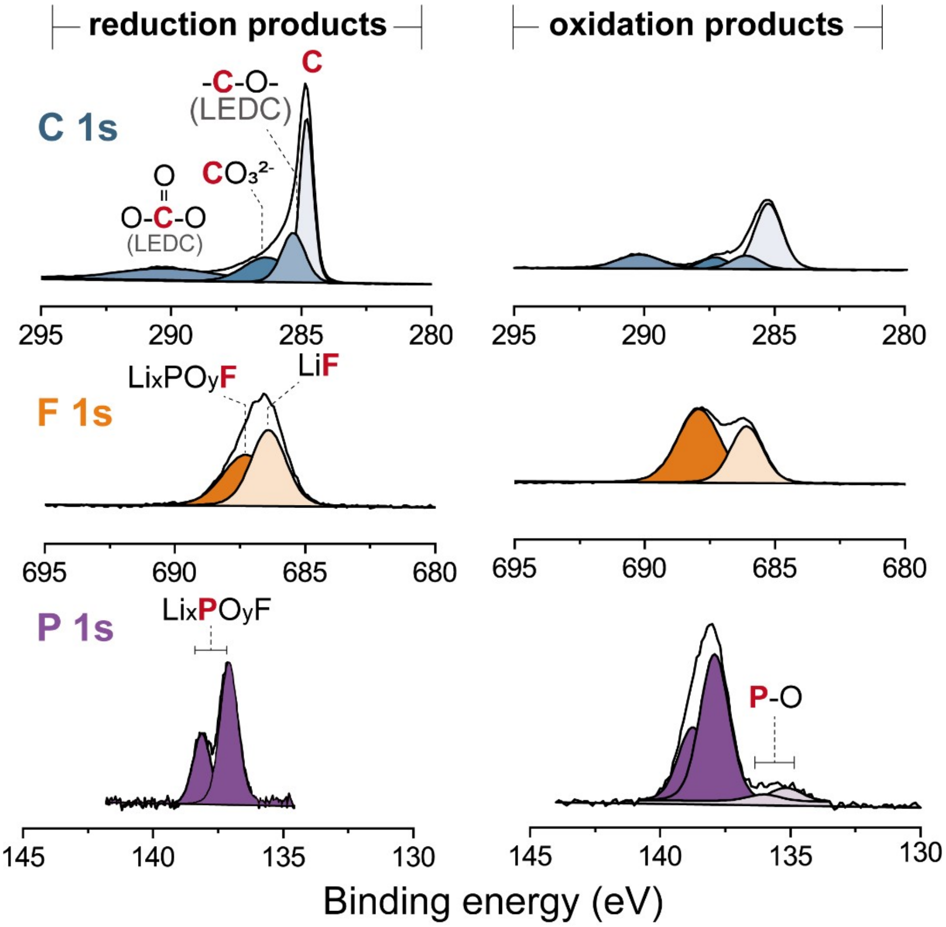

Fig. S4. XPS spectra of C 1s, F 1s and P 2p for the reduction and oxidation products of controlled electrolytes.

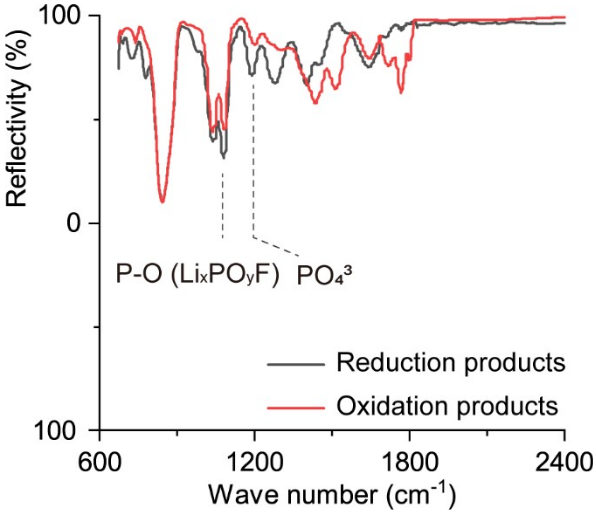

Fig. S5. ATR-FTIR spectrum of the reduction and oxidation products of controlled electrolytes.

As shown in Fig. S5, the characteristic peaks of their reduction and oxidation products are similar to that of LiDFBOP-added electrolytes. However, the intensity of peaks related to P-O and PO_4^{3-} is weaker than that of LiDFBOP-added electrolytes. It means that one of the main products of the reduction and oxidation of LiDFBOP are LixPOyF and PO_4^{3-}, respectively.

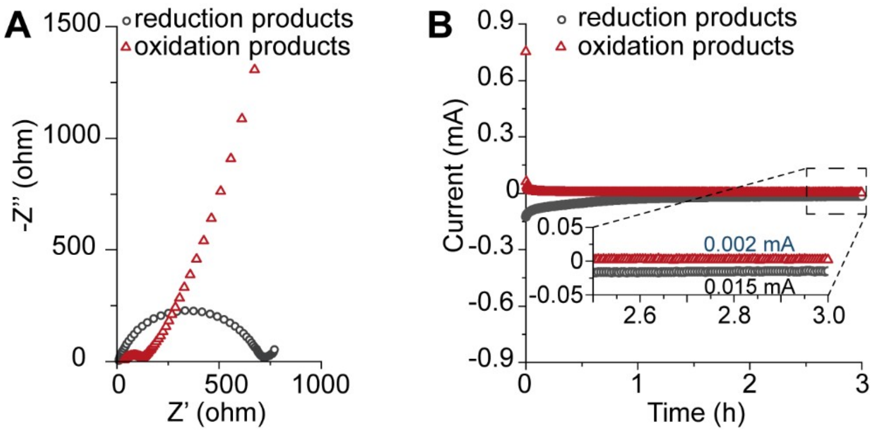

Fig. S6. Interface stability of the different SEI layers dominated by the reduction and oxidation products of the LiDFBOP-added electrolyte. (A) Electrochemical impedance spectroscopy (EIS), (B) Leakage current.

According to the results of the EIS test (Fig. S5A), the radius of the oxidation curve is smaller than that of reduction products, indicating the oxidation products in favor of the charge transfer process. It agrees with the previous report that phosphate has high Li^+ ion conductivity. Meanwhile, the organic compounds with favorable viscoelasticity in the oxidation products enable the SEI layers to adhere to the electrode surface firmly, suppressing side reactions and decreasing the leakage current (Fig. S5B).

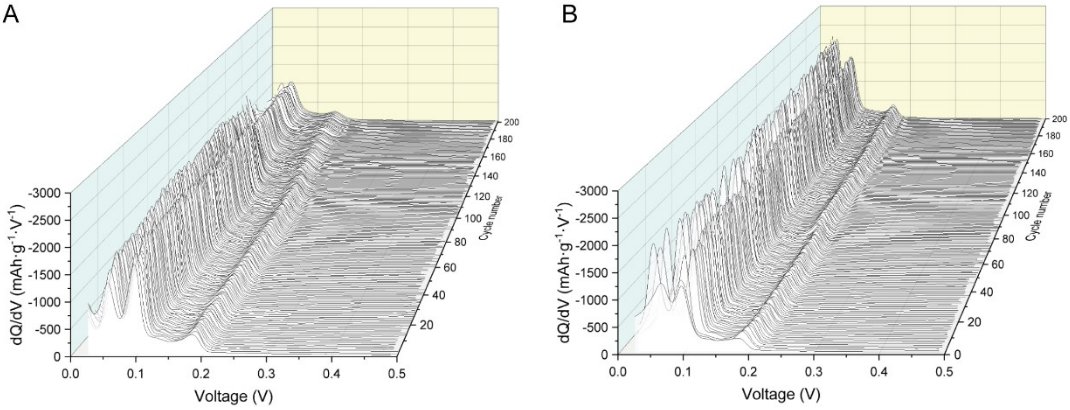

Fig. S7. The 3D discharge-related dQ/dV curves of cells with (A) the controlled SEI and (B) the LiDFBOP-added SEI during the first 200 cycles at 0.5 C.

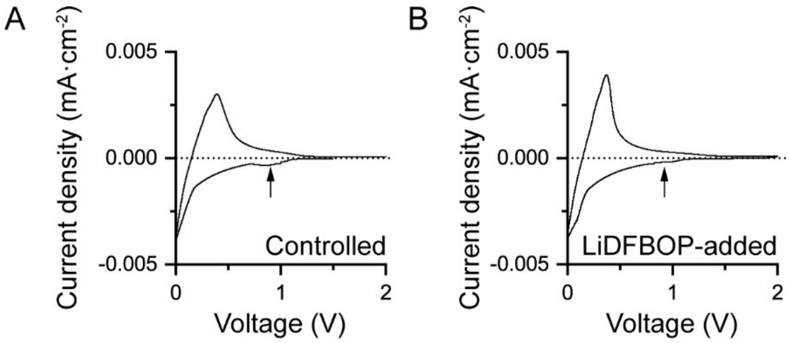

Fig. S8. The cyclic voltammogram plot of cells with the designed SEI layers formed by (A) controlled and (B) LiDFBOP-added electrolytes at the scan rate of 0.5 mV/s.

As shown in Fig. S8, the CV plot of controlled cells shows an obvious reduction peak at about 0.9 V, which is attributed to the reduction of EC. However, this peak is absent in the CV plot of cells with LiDFBOP-added electrolytes. It means that our designed gomphosis-like SEI layers offered effective protection, avoiding the contraction of electrodes and electrolytes and restraining the further decomposition of electrolytes.

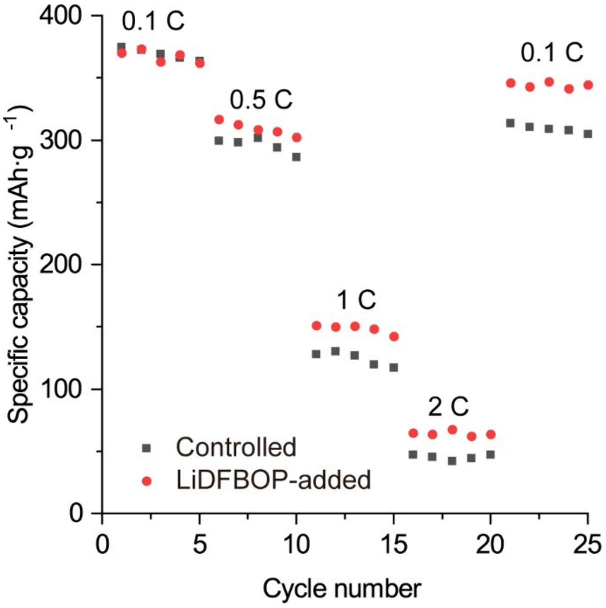

Fig. S9. The charge capability plot of cells with the designed SEI layers formed by controlled and LiDFBOP-added electrolytes.

Fig.S9 illustrates the rate-capability results of two different cells. At the charge rate of 0.1 C, the specific capacity of both cells is about 360 mAh·g^{-1}. However, with the increase in charge rate, the cells with LiDFBOP-added electrolytes show a higher charge capacity. Especially the charge rate back from 2 C to 0.1 C, the charge capacity of cells with LiDFBOP-added electrolytes remains about 350 mAh·g^{-1}, whereas the capacity of controlled cells is just about 310 mAh·g^{-1}. According to the discussion in the manuscript, it benefits from wedge-shape-distribution phosphates in LiDFBOP-added SEI that provide Li^{+} with a high conductivity diffusion path.