Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Electronic Supplementary Information

Effect of electrolyte on the nanostructure of the solid electrolyte interphase (SEI) and performance of lithium metal anodes

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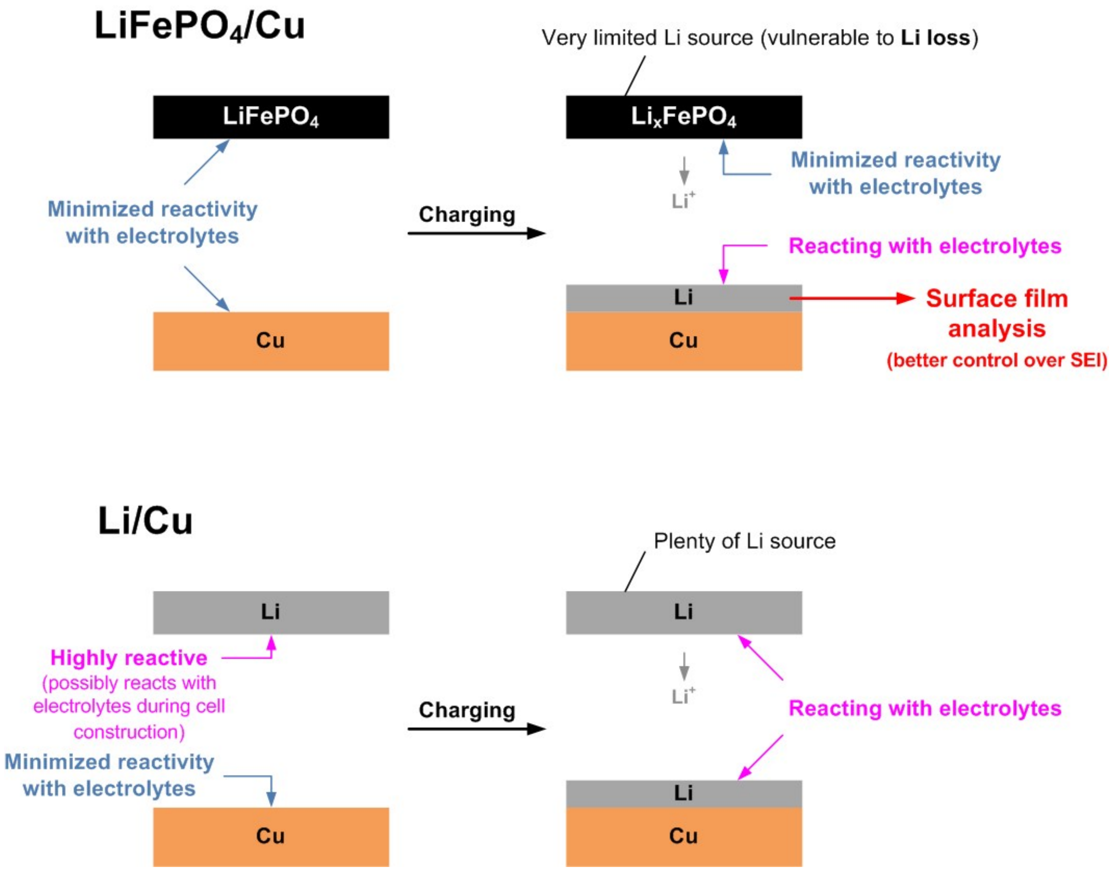

Fig. S1. A general concept of $LiFePO_4$/Cu cell to analyze the surface of lithium metal.

Contrary to other cells, $LiFePO_4$/Cu cells allow the generation of lithium metal in-situ, such that the electrolytes only react with the strongly reducing lithium metal upon initial plating. This prevents reaction of the electrolyte with the lithium metal electrodes during cell construction and affords better control over SEI formation.

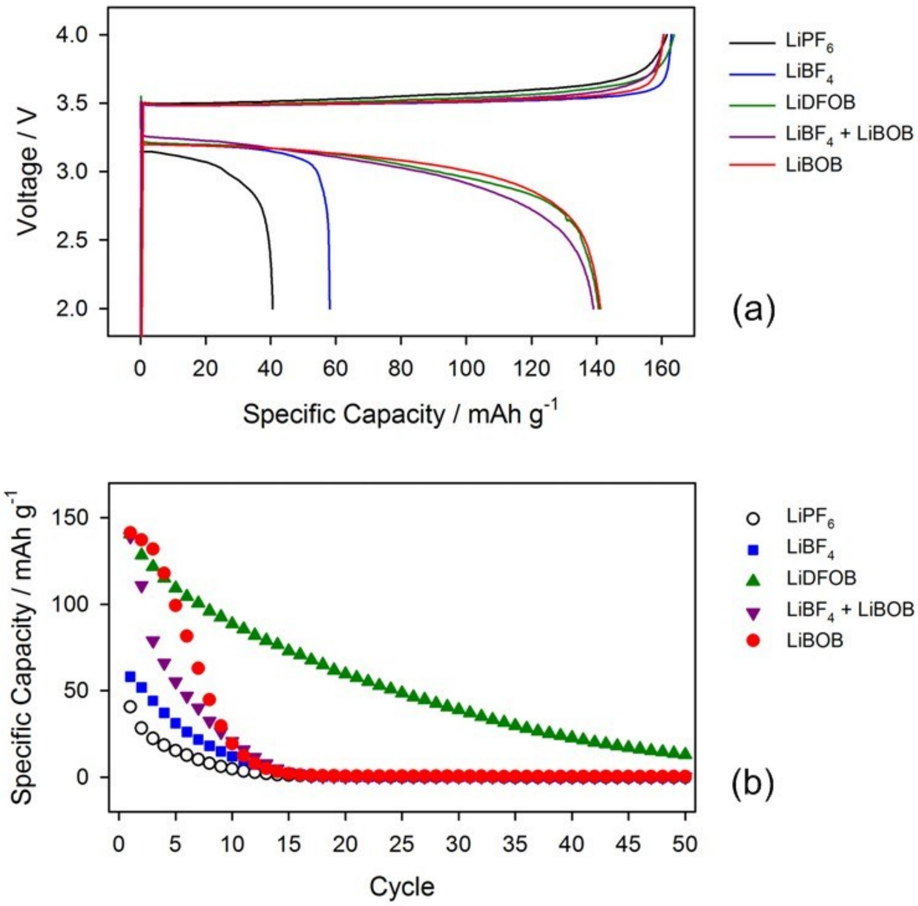

Fig. S2. Comparison of the (a) 1st lithium plating/stripping profile and (b) stripping capacity *vs.* cycle number obtained from $LiFePO_4$/Cu cells using the investigated electrolytes.

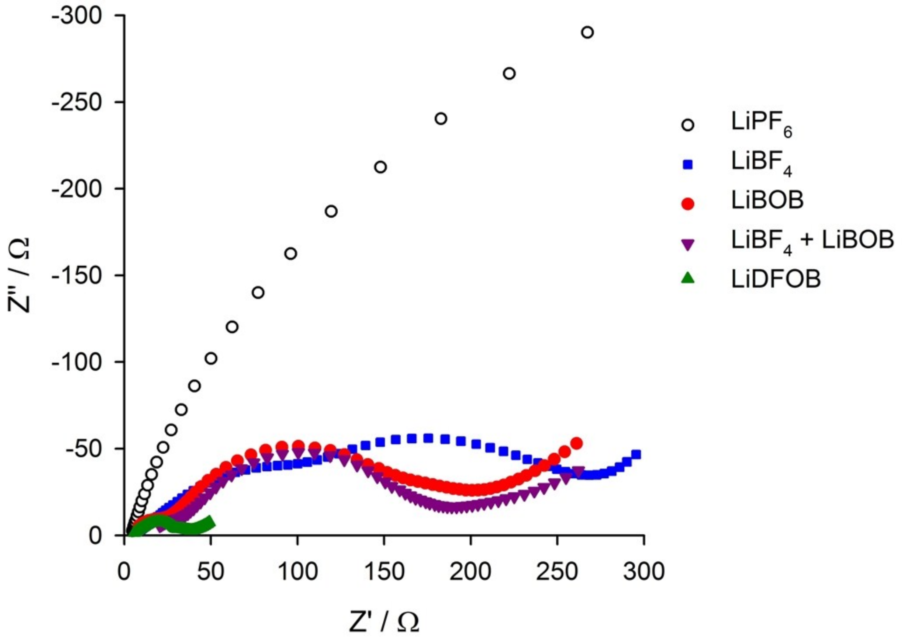

Fig. S3. The Nyquist plots obtained from the Li/Li symmetric cells, in which lithium electrodes were generated from $LiFePO_4$/Cu cells containing the investigated electrolytes.

Electrochemical impedance spectroscopy (EIS) was conducted on Li/Li symmetric cells at 25°C. Li/Li cells for EIS were prepared from two identical $LiFePO_4$/Cu cells cycled with the procedure mentioned above until the 10th lithium plating. The cells were then disassembled in an argon glove box and Li/Li cells were assembled with a PP/PE/PP separator using the same electrolyte and allowed to equilibrate for 2 hours. The cells were tested using a Biologic VSP in a frequency range from 100 kHz to 100 mHz with a 5 mV amplitude excitation.

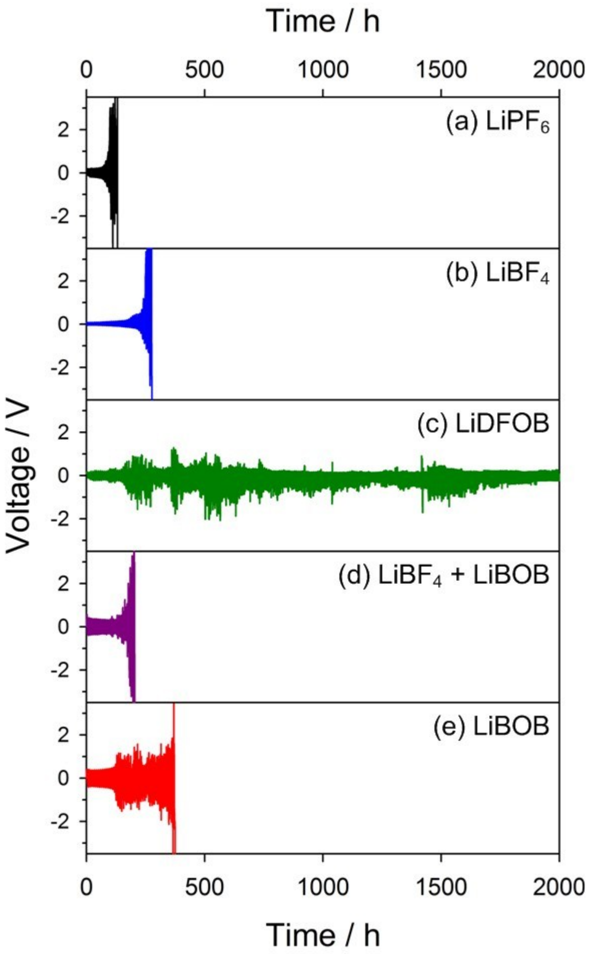

Fig. S4. Galvanostatic cycling results of Li/Li symmetric cells with current density of 0.5 mA cm^{-2} and limited charge/discharge capacity of 2 mAh cm^{-2}.

2032-type coin cells containing two identical lithium electrodes and two separators (PP/PE/PP and glass fiber) were assembled to perform electrochemical testing. Li/Li cells were cycled with current density of 0.5 mA/cm^2 and limited charge/discharge capacity of 2 mAh/cm^2. A 3-hour rest period was also inserted at the beginning of each cycling protocol to ensure uniform wetting of all cell components.

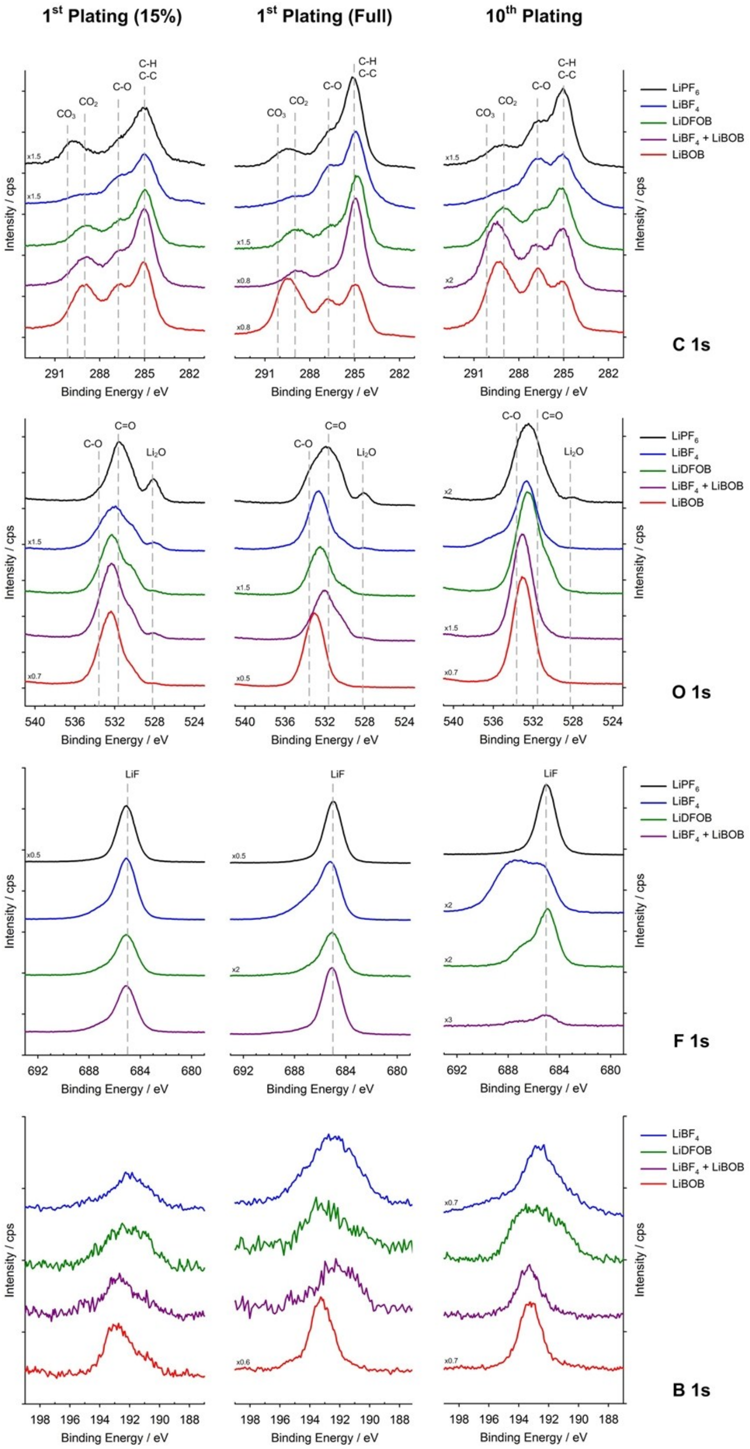

Fig. S5. XPS spectra obtained from lithium plated using the investigated electrolytes.

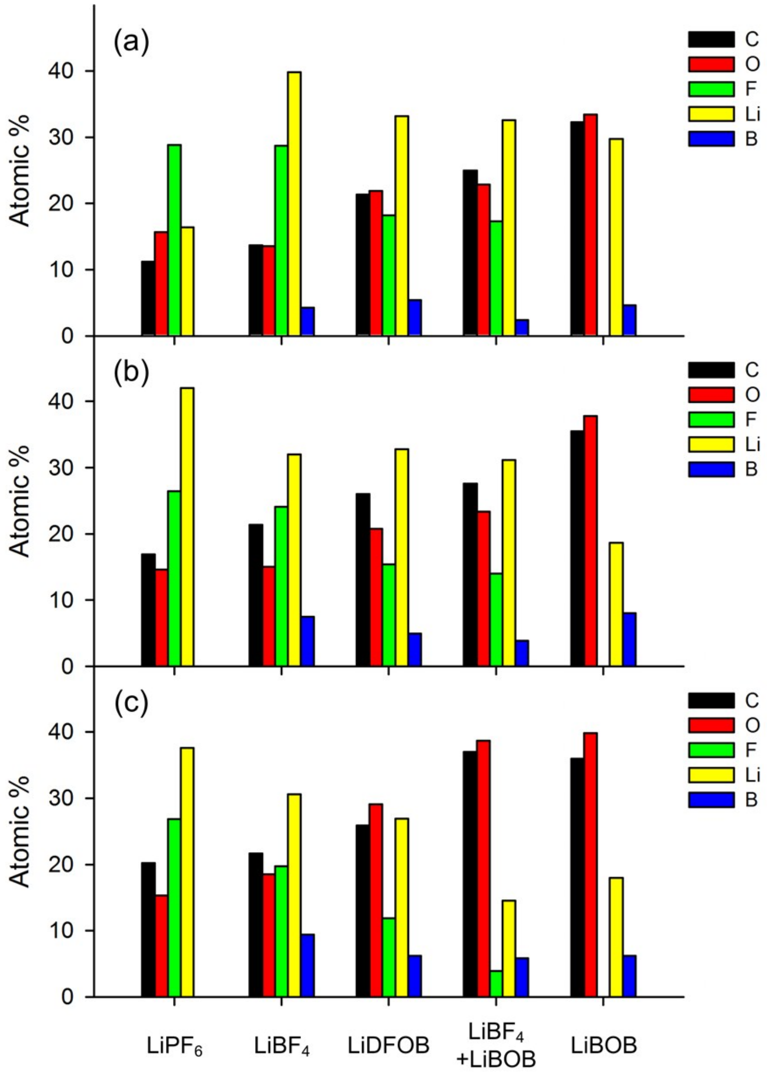

Fig. S6. Corresponding relative atomic concentrations from XPS spectra for lithium at the (a) 15% of 1st plating, (b) full 1st plating, and (c) 10th plating.

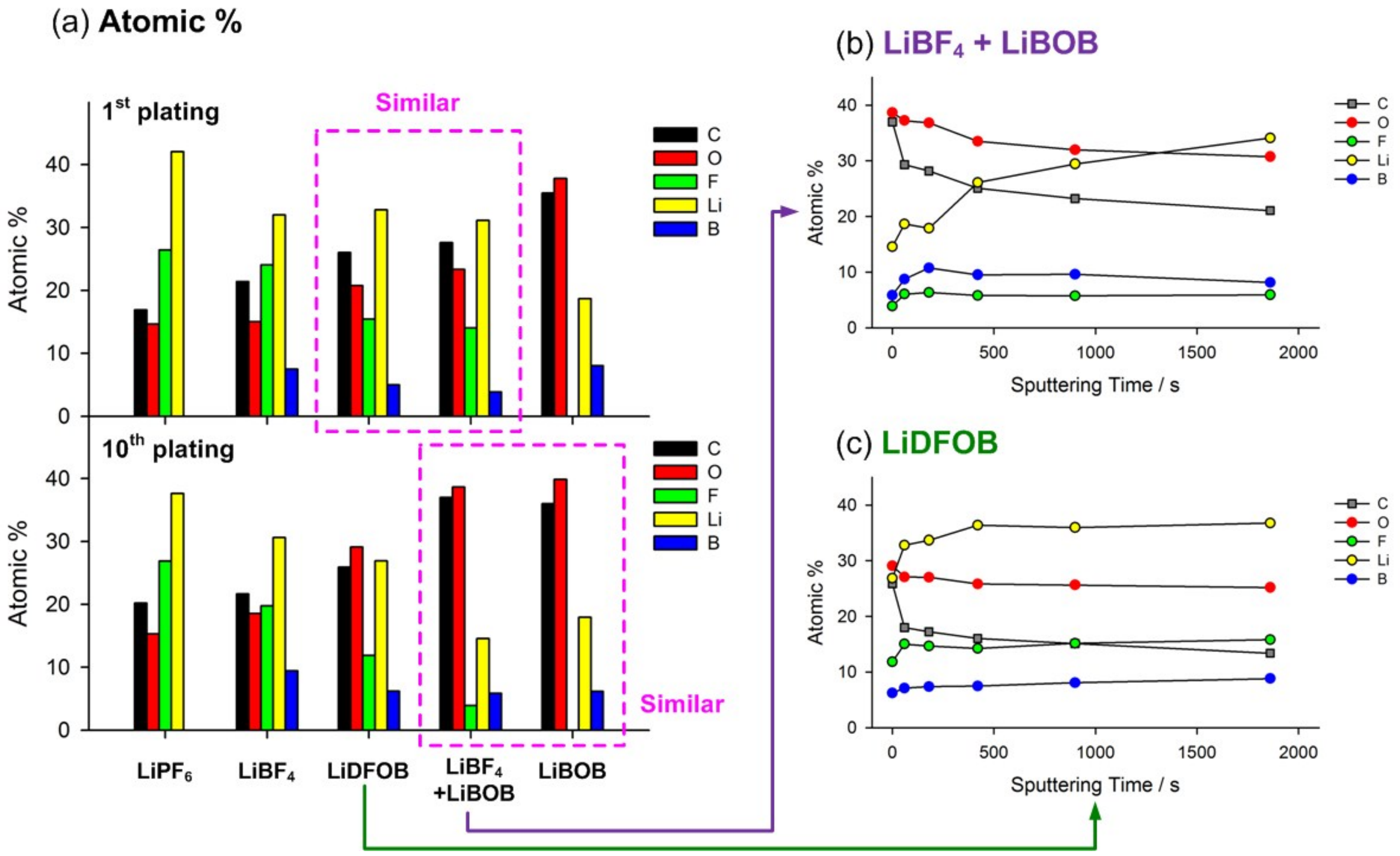

Fig. S7. (a) Corresponding relative atomic concentrations from XPS spectra and the relative XPS atomic concentration profile upon argon sputtering of lithium plated from (b) 0.6 M $LiBF_4$ + 0.6 M LiBOB in EC:EMC and (c) 1.2 M LiDFOB in EC:EMC.

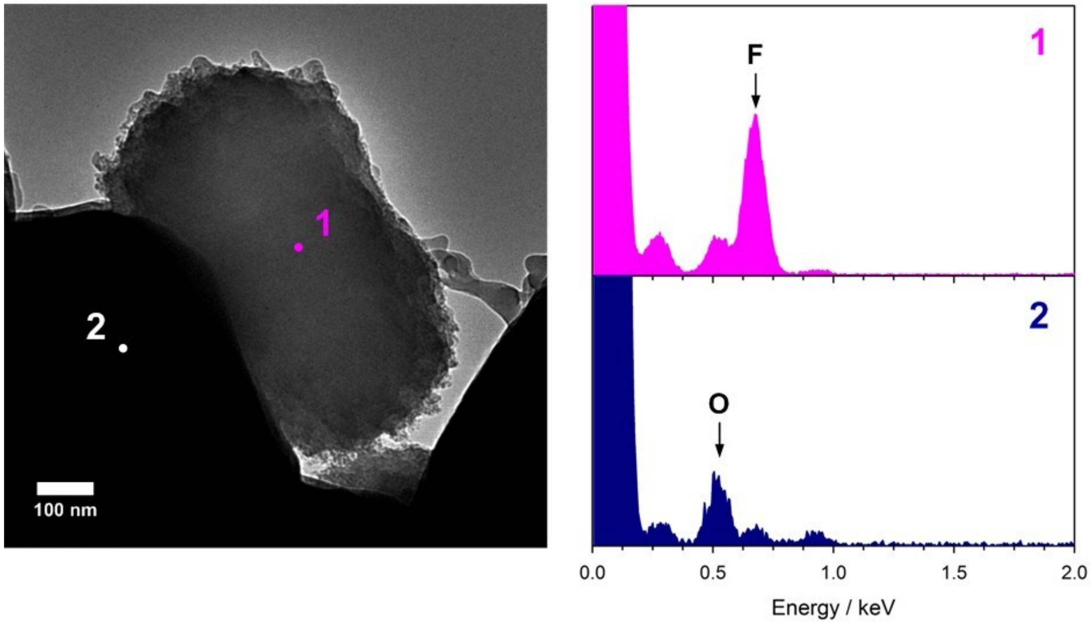

Fig. S8. EDX spectra of lithium plated from 0.6 M $LiBF_4$ + 0.6 M LiBOB in EC:EMC.

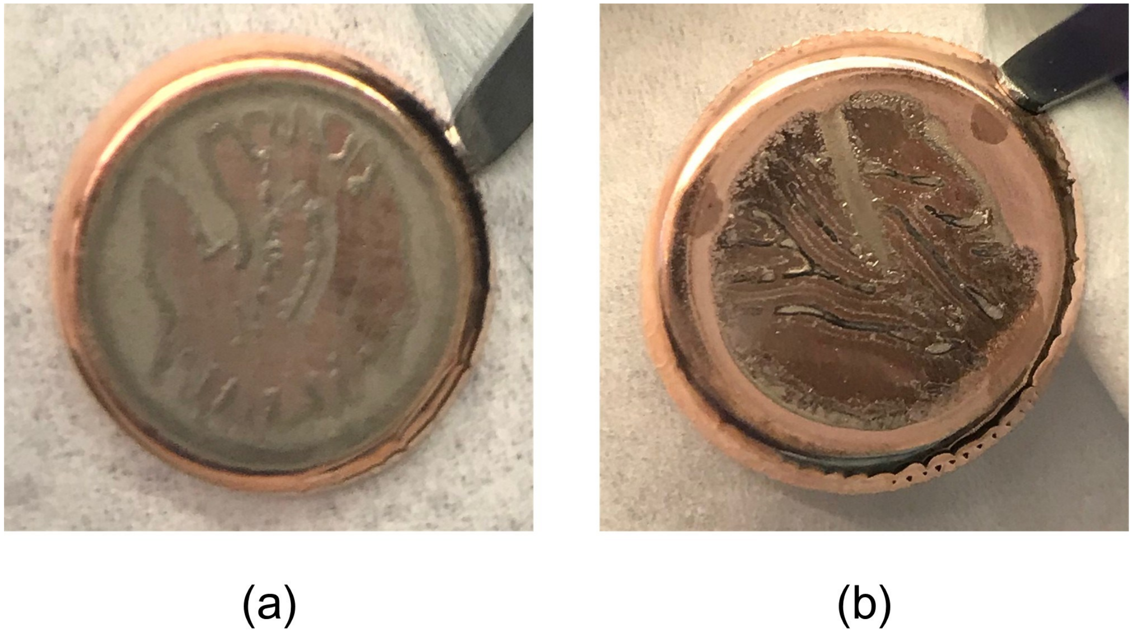

Fig. S9. Images of copper electrodes plated from (a) 1.2 M $LiPF_6$ in EC:EMC and (b) 1.2 M LiDFOB in EC:EMC after the 1st lithium plating/stripping cycle.

After 1st stripping, mossy lithium is still remained on copper electrode for the $LiPF_6$ electrolyte, in accordance with poor efficiency. On the other hand, all the lithium on the copper electrode for the LiDFOB electrolyte has stripped almost completely.

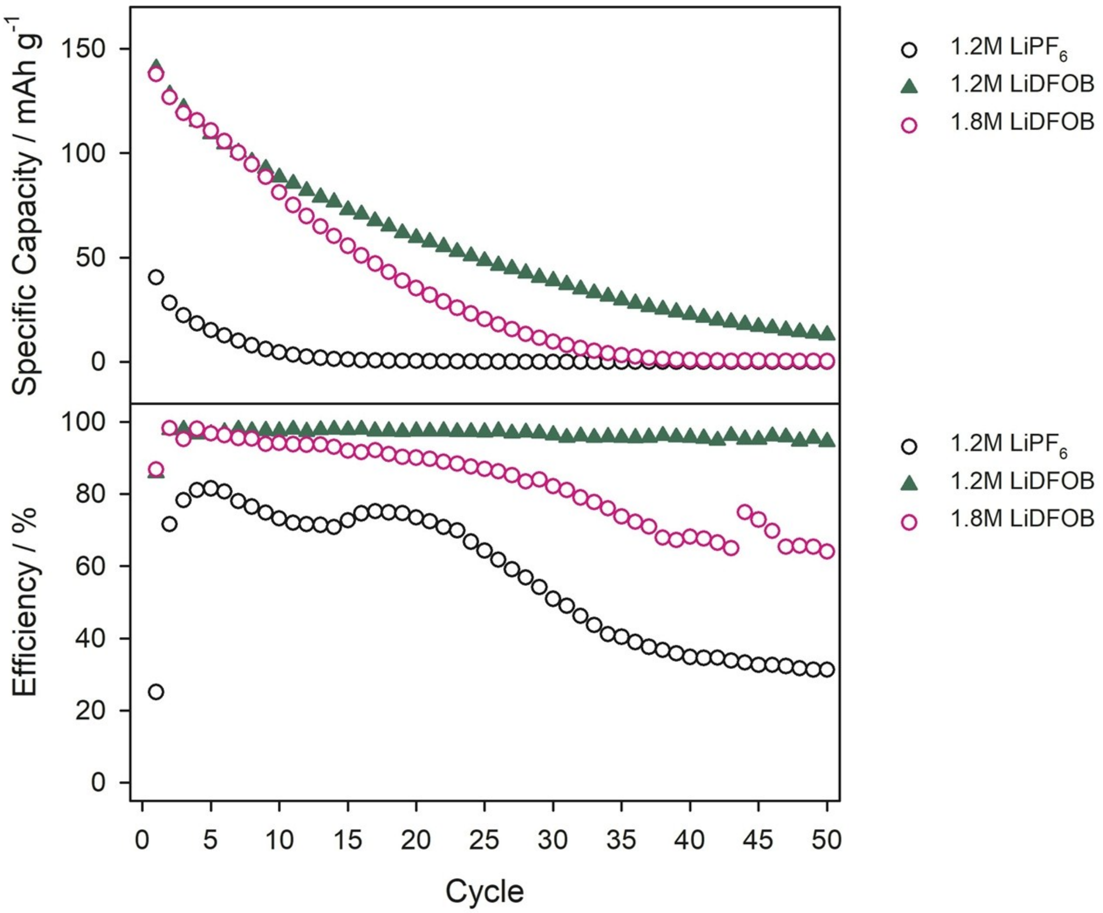

Fig. S10. Comparison of the (a) stripping capacity and (b) efficiency *vs.* cycle number obtained from $LiFePO_4$/Cu cells using the investigated electrolytes.

The change of concentration for LiDFOB salts does not affect the electrochemical performance of $LiFePO_4$/Cu cells significantly.