

Supporting Information

Synergetic effect of ethyl methyl carbonate and trimethyl phosphate on BF_4^- intercalation into graphite electrode

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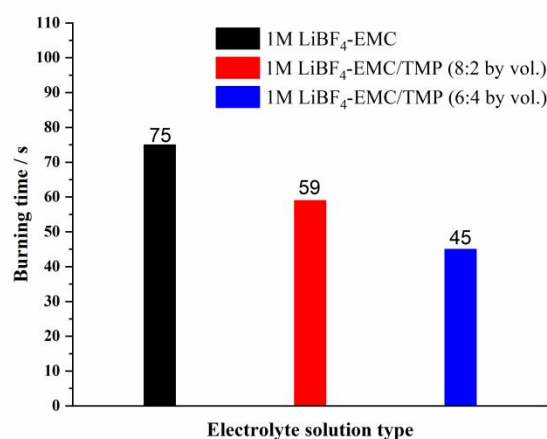


Figure S1. Burning times of different electrolyte solutions.

(Measurement details were the same as the those in the reference (ACS Appl. Energy Mater.

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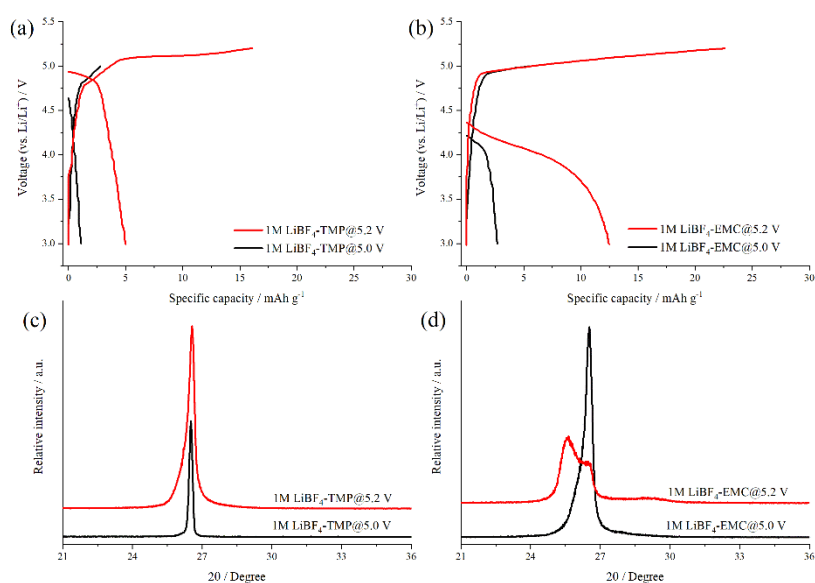


Figure S2. Initial galvanostatic charge-discharge curves of graphite electrodes and *ex situ* XRD

patterns of graphite electrodes during the galvanostatic charge-discharge of Li/graphite cells in the

electrolyte solutions of 1M LiBF₄-TMP (a) and (c), 1M LiBF₄-EMC (b) and (d), at different

cut-off voltage, respectively.

Figure S2 compares the 1 st-cycle galvanostatic charge-discharge curves of graphite electrodes in the electrolyte solutions of 1M LiBF₄ dissolving in the pure solvent of TMP or EMC, and the corresponding *ex situ* XRD patterns of graphite electrodes at different cut-off voltage, respectively. It is evident that elevating the cut-off voltage can easily increase the charge capacity of graphite positive electrode in 1M LiBF₄-TMP or -EMC. However, different shape of the discharge curves may illustrate the different extent of BF₄⁻ intercalation into graphite in 1M LiBF₄-TMP or -EMC at the same cut-off voltage of 5.2 V. And the *ex situ* XRD patterns of graphite electrodes in 1M LiBF₄-TMP or -EMC at different cut-off voltage in **Figure S2** (c) and (d) may demonstrate that BF₄⁻ intercalation into graphite doesn't change the structure of graphite layers from 1M LiBF₄-TMP at the cut-off voltage of 5.0 V or 5.2 V, which indicates the extremely difficult entrance of BF₄⁻ into the graphite electrode, different from the case of 1M LiBF₄-EMC at different cut-off voltage.

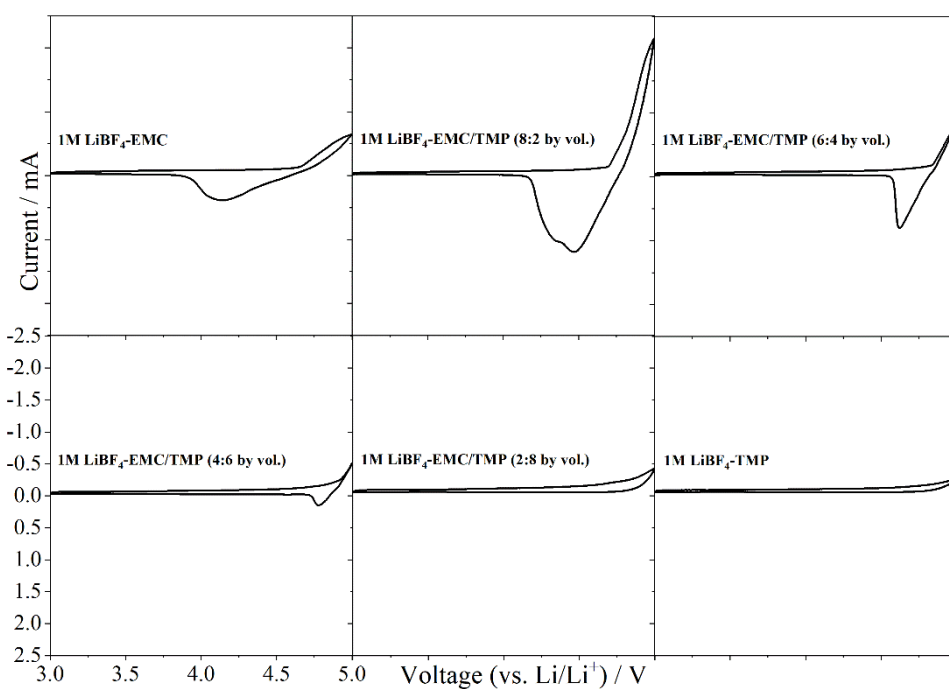


Figure S3. Cyclic voltammograms of graphite electrodes in the electrolyte solutions of 1M

LiBF₄-EMC/TMP at the first cycle.

(**Measurement:** Cyclic voltammetric measurements (potential range: 3 to 5 V (vs. Li/Li⁺), scan rate: 1 mV s⁻¹) of the graphite electrodes were operated by electrochemical workstation (CHI700D, Shanghai, China, Chenhua Co. Ltd.) on three-electrode cells in which Li chip was used as reference and counter electrodes.)

The insights obtained from the galvanostatic charge-discharge tests of **Figure 1** may be verified by cyclic voltammetric studies. From the **Figure S3**, the area surrounded by the curve first enlarges and then shrinks along with the rising TMP proportion, may reflect that the increased/decreased amounts of solvated-BF₄⁻ take part in the intercalation/de-intercalation process, respectively. And in the TMP solvent, BF₄⁻ hardly intercalates in graphite. A pronounced cathodic peak appears in the 1M LiBF₄-EMC/TMP (8:2 by vol.), which means a considerable amount of anions can be de-intercalated from graphite electrode. Combined with the largest area surrounded by the curve using the 1M LiBF₄-EMC/TMP (8:2 by vol.), the enhancement effect on BF₄⁻ intercalation into the graphite by the mixed solution also can be verified. All these facts agree with the results of **Figure 1**.

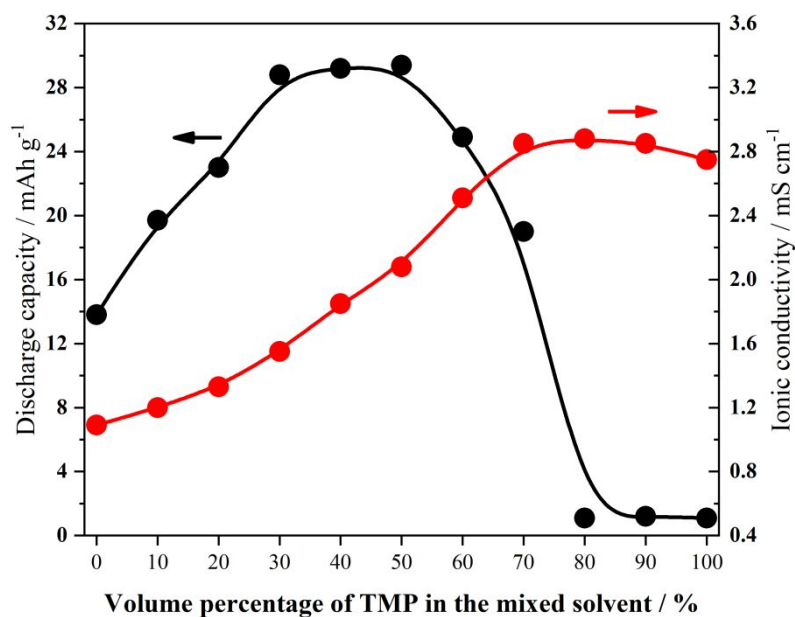


Figure S4. Relationship curves between first cycle discharge capacity of graphite electrode, ionic conductivities of the electrolyte solutions and the TMP content in 2M LiBF₄-EMC/TMP.

Figure S4 displays the relationship curves between 1-st cycle discharge capacities of graphite positive electrode, ionic conductivities of the electrolyte solutions and the TMP content in 2M LiBF₄-EMC/TMP. The change trends and the curves shape are similar with the **Figure 4 (a)** directly presenting the synergetic effect of two solvents on BF₄⁻ storage at graphite electrode in 1M solutions, except for the discharge capacity maximum point shifting to higher TMP content. This is because there are more Li⁺-BF₄⁻ pairs in the concentrated solution and then more TMP is needed split off them.