

Supporting materials

The structure of LiBOB, VC and PP13TFSI are shown in Fig.s1a, function of SEI on surface of carbon electrode is shown in Fig.s1b.

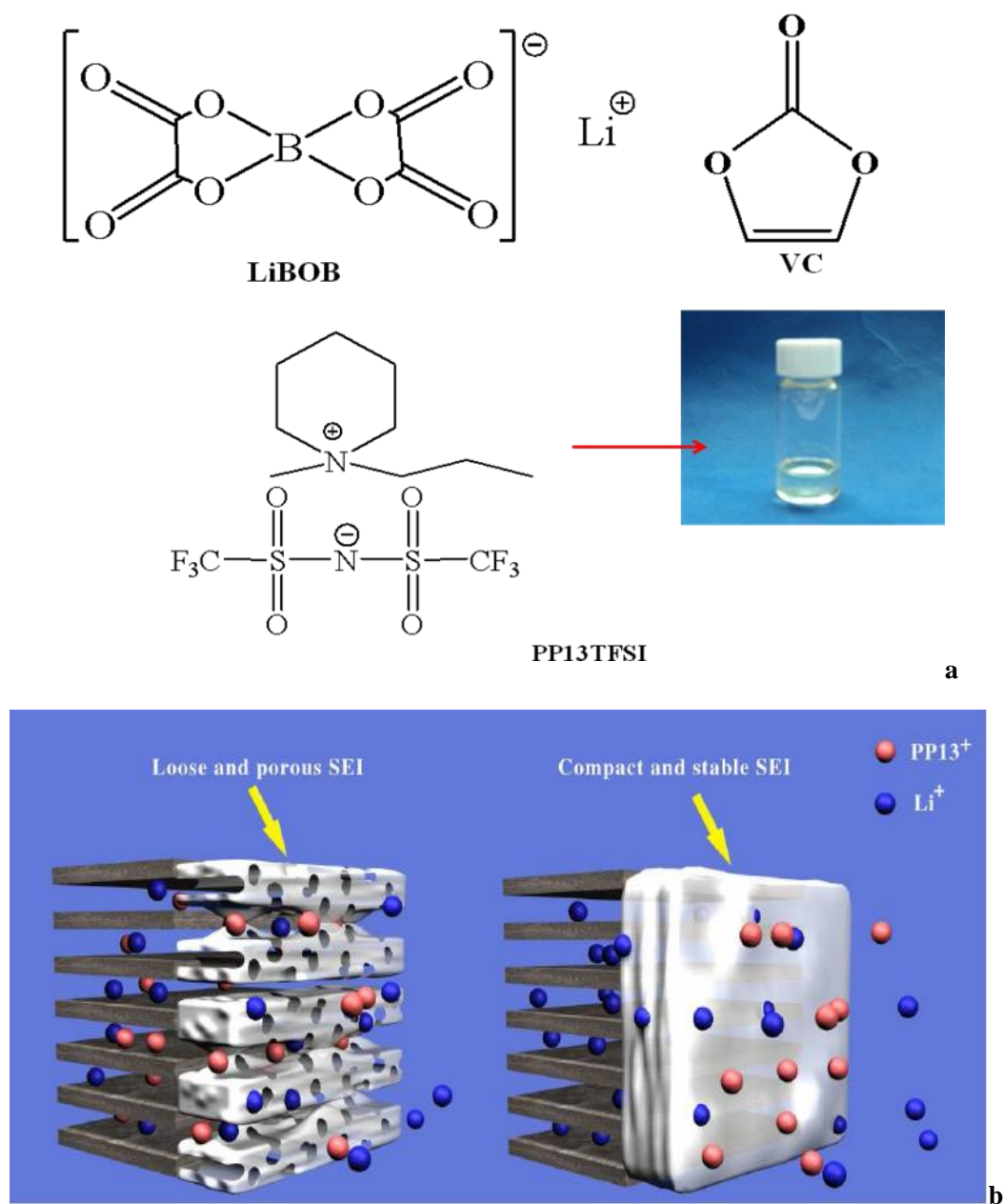


Fig.s1 The structures of LiBOB, VC and PP13TFSI (a) and function of SEI on surface of carbon electrode (b)

The Fig.s2 shows the mechanism of VC and LiBOB forming SEI .As can be seen, the main component of SEI forming by additives is semi carbonate. The structure of VC has the C=C double bond, when VC forms SEI film, the product of VC decomposition can form containing “-ROCOOLi-“polymer compound. It can make the SEI film has better glutinosity and flexibility, which can restrain the changes of electrode during charge-discharge course.

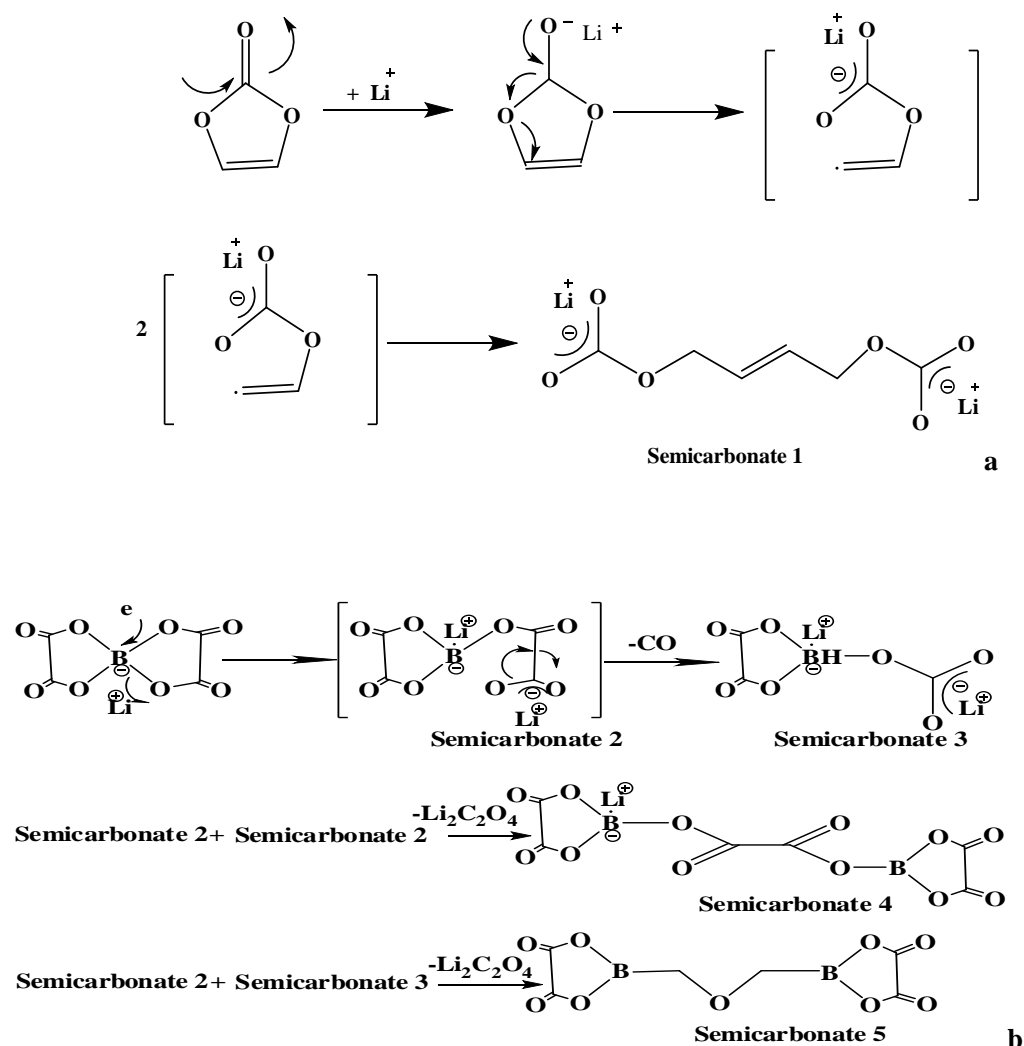


Fig.s2 The mechanism of VC (a) and LiBOB(b) forming SEI

Fig.s3 gives the SEM images of SEI forming by VC (a) and LiBOB (b) additive on carbon electrode. As can be seen, VC additive forms compact and thick film on carbon electrode (because of forming “-ROCOOLi-”polymer), while LiBOB forms thin and compact film.

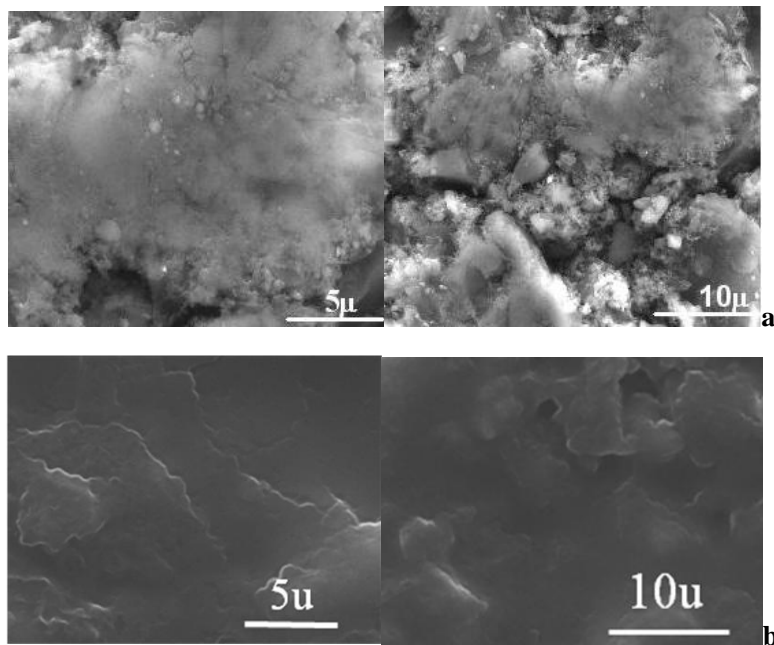


Fig.s3 The SEM images of SEI forming by VC (a) and LiBOB (b) on carbon electrode

Fig.s4 show the cyclic voltammogram (a) and cycle (b) plots of the Li/C cell using only VC-containing mixed electrolyte .As can be seen, the largely decomposition of VC(started at 1V) in first cycle leads to the lower coulomb efficiency in 1st cycle (lower than 70%). So we design the VC-LiBOB binary additive containing mixed electrolytes. One side , the LiBOB can partly restrain VC largely decomposition, on the other hand ,the composite SEI formed by VC and LiBOB will be compact and thick than single one [SEE the date of elemental concentration (%) of SEI on electrode using different additives containing mixed electrolyte in paper]

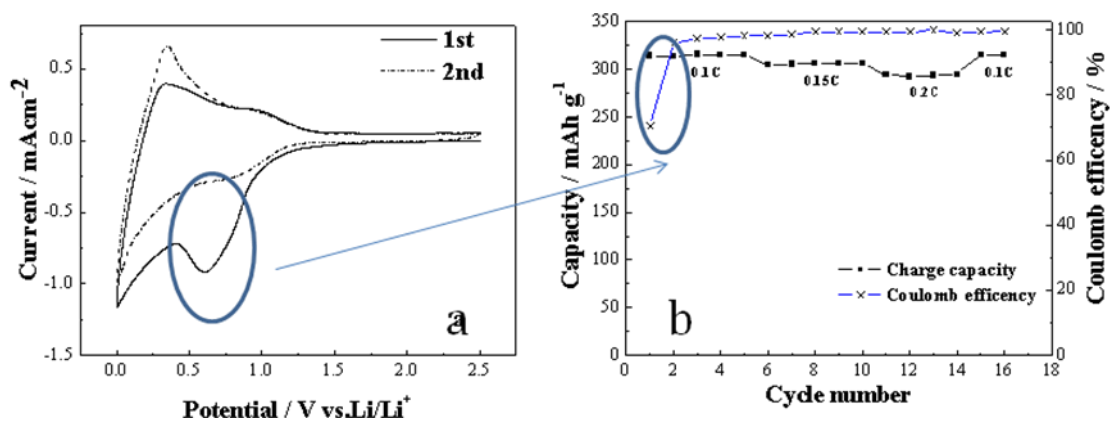


Fig.s4 The cyclic voltammogram and cycle plots of the Li/C cell using only VC-containing mixed electrolyte

Fig.s5 shows the voltage-capacity plots of the cell using mixed electrolyte with/without binary additives. The SEI also can be proved by the voltage-capacity plots of the cell with binary additives containing mixed electrolyte in the first cycle, the two voltage plateaus of 1.75 V and 0.8 V is associated with the decomposition of LiBOB and VC, from the second cycle, the two voltage plateaus disappear, this effectively prove the well SEI forming progress in the first cycle, while the cell with the additive-free mixed electrolyte show a highly voltage plateau for decomposition of electrolytes in first cycle. This is in according with the cyclic voltammogram plots above mentioned.

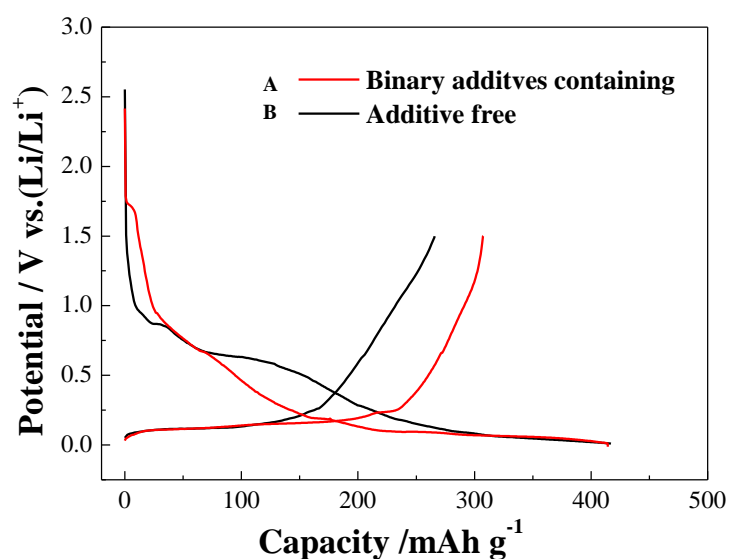
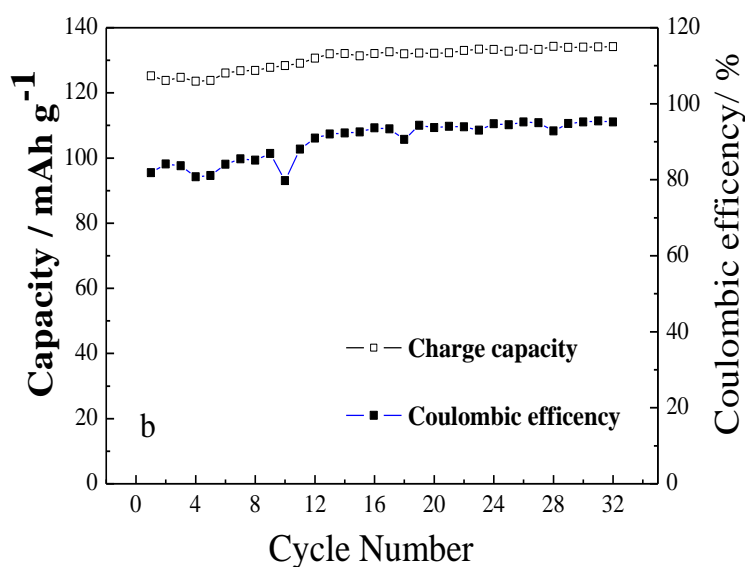
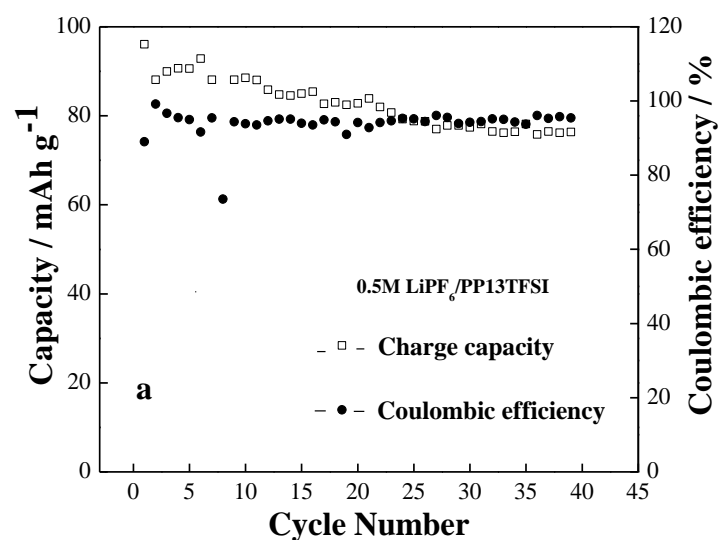


Fig.s5 The first voltage-capacity plots of the Li/hard carbon-graphite cell using mixed electrolyte with/without binary additive

We also test the Li/LiFePO₄ cell using the binary-additive containing mixed electrolytes. Fig.s6 gives the cycle number vs. capacity plots of the cell at 0.1C rate. Although the first charge and discharge capacities are only 137 mAh g⁻¹ and 123 mAh g⁻¹ respectively, but from the second cycle, the reversible capacity and coulombic efficiency increase obviously, even after 35th cycle, the cell is able to deliver capacity of 130 mAh g⁻¹ with coulombic efficiency close to 100%. This is due to the binary additive improving the interface contact between the electrolyte and electrode. While the cell using mixed electrolyte without additives show poorly coulombic efficiency, this is due to the continuously reaction between the electrolyte and electrode. The Li/LiFePO₄ cell using pure IL-based electrolyte system shows lower reversible capacity (~90mAh g⁻¹). The performance of the Li/LiFePO₄ cell are also enhanced by the binary additives, the Li/LiFePO₄ cell using the binary additive containing mixed electrolyte shows the acceptable reversible capacity and coulombic efficiency.



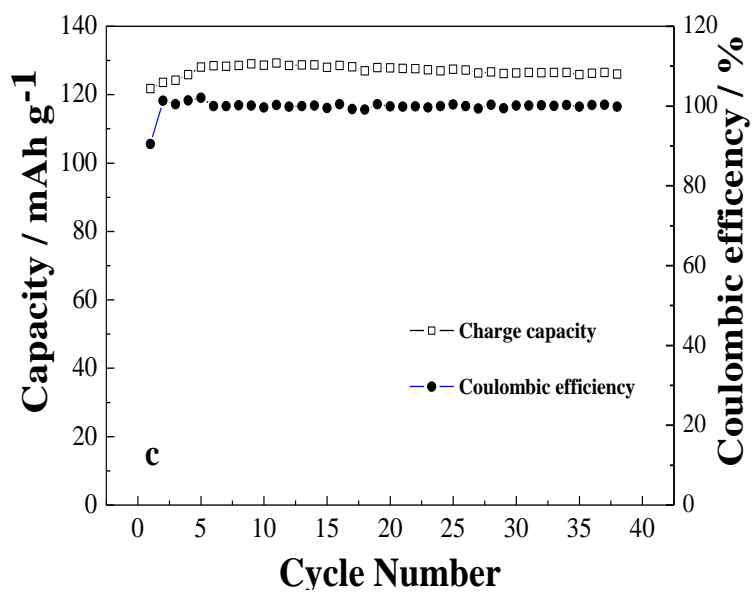


Fig.s6 The cycle of performance of Li/LiFePO₄ cell using pure ionic liquid (a), additive free (b) and the binary additives (c) containing mixed electrolyte at room temperature