Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

A Fire-retarding Electrolyte using Triethyl Phosphate as Solvent for Sodium-ion Batteries

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The electrolyte solvents viz., TEP, TMP, tetraglyme, PC, and DEC are tested for the corrosion behaviour of sodium metal and the results are shown in Fig. S1(a), (b), and (c). More specifically, a piece of 18.5 mg sodium metal is dropped into the glass bottles, each of which contains 3 ml electrolyte solvent. The status of the sodium metal was recorded after every 1 h, 1 day, and 1 week. After an hour of observation (shown in Fig. S1(a)), noticeable reaction is registered in the TEP solution, the sodium piece partially dissolved and there is obvious gas emission from the surface of the sodium metal. It can also be observed that the tetraglyme solution shows slight color change, indicating possible chemical reaction with sodium metal. As for DEC solution, a noticeable layer of black-colored coating is observed. Fig. S1(b) shows the condition of the sodium metal and solvents after one day and it can be observed that the sodium metal in TEP fully dissolved while the one in TMP partially dissolved. It can also be noticed that sodium metal further reacted with tetraglyme and DEC. However, the sodium kept in PC solution seems still at a stable state. It can be seen in Fig. S1(c) that after one week, the sodium metal in both TEP and TMP fully dissolved and precipitant is observed in both of the solutions. The color of tetraglyme is darkened and the sodium metal in DEC is fully covered with a black colored coating. The PC solution also shows a bit of color change, indicating that the sodium metal is not perfectly stable in PC solution as well. According to the above results, we can see that TEP is the most reactive one against sodium metal among all the electrolyte solutions tested. Furthermore, an excessive amount of sodium metal (2 g) is dropped in 3 ml of TEP solution (shown in Fig. S1(d), (e), and (f)). It can also be noticed that the final product of the reaction of TEP solvent with excessive Na metal is a gel-like compound.

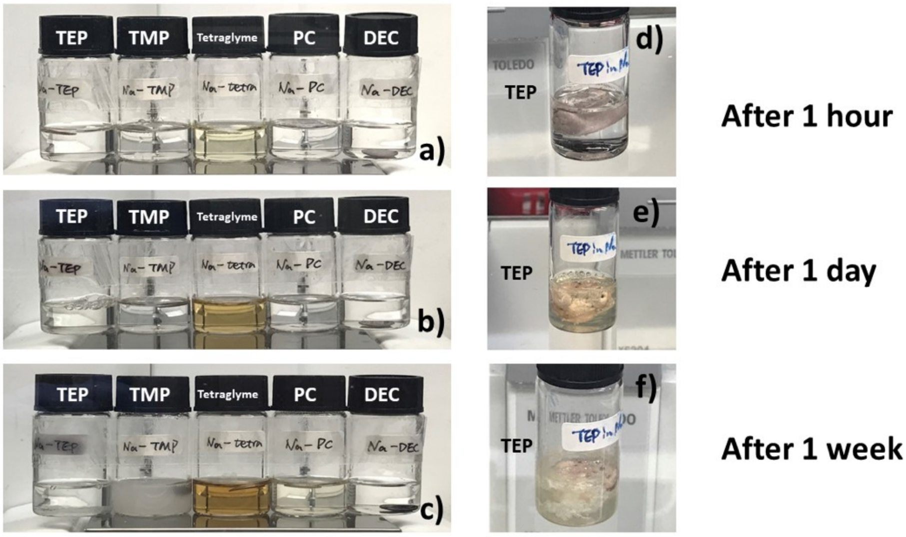

Fig. S1. Sodium metal corrosion test of TEP, TMP, tetraglyme, PC, and DEC after (a) 1 hour, (b) 1 day, and (c) 1 week (18.5 mg in 3 ml of solution). Excess amount of sodium metal (2 g) was also tested in TEP solution (3 ml) after (a) 1 hour, (b) 1 day, and (c) 1 week.

From the results shown in Fig. S1, it can be noticed that different solvents shows different reactivity with sodium metal and amongst all the electrolyte solvents investigated, TEP shows the highest reactivity with sodium metal and the energy diagram shown in Fig. S2 can explain this phenomenon. Fig. S2 shows the electrolyte reduction level at negative potential and electrolyte oxidation level at positive potential. If the reduction level at negative potential of the electrolyte is lower than the energy level of Na metal, as is shown in Fig. S1(a), the electrons from the Na metal will move towards the electrolyte, leading to chemical reactions on the surface of the Na metal. Some of these reactions may form an interlayer between the Na metal and the electrolyte and block the contact between the electrolyte and the solvent, preventing further corrosion of the sodium metal. This phenomenon can be seen in Fig. S2(b), which may also explain the black-colored interlayer shown with DEC in Fig. S1. However, if this surface reaction cannot form any stable interlayer, the reaction between Na metal and electrolyte will continue and finally deplete one of the reactants, which explains why the Na metal piece fully dissolves in the TEP solvent as shown in Fig. S1.

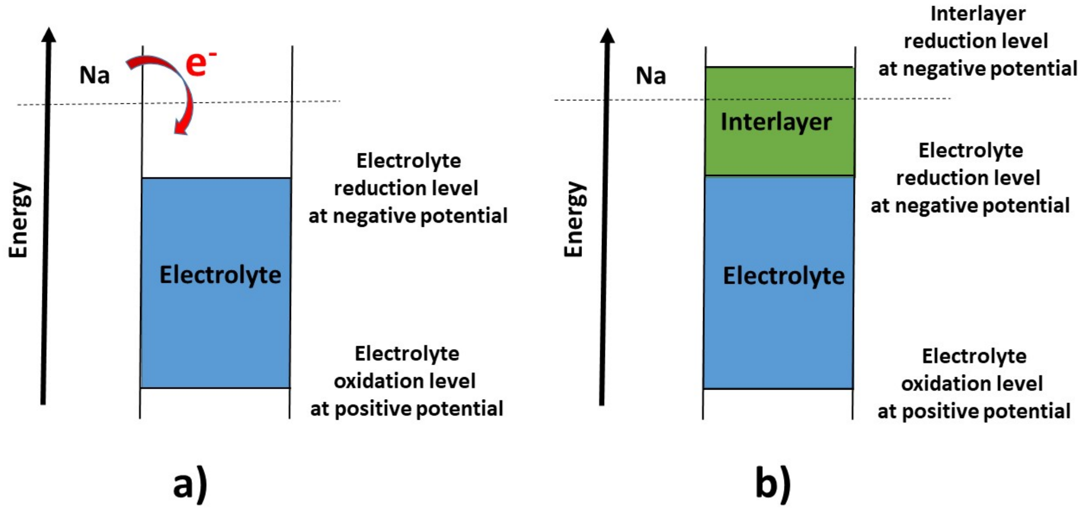

Fig. S2. Energy diagram of (a) Na, electrolyte with low electrolyte reduction level at negative potential without interlayer formation; (b) Na, electrolyte with low electrolyte reduction level at negative potential with interlayer formation.

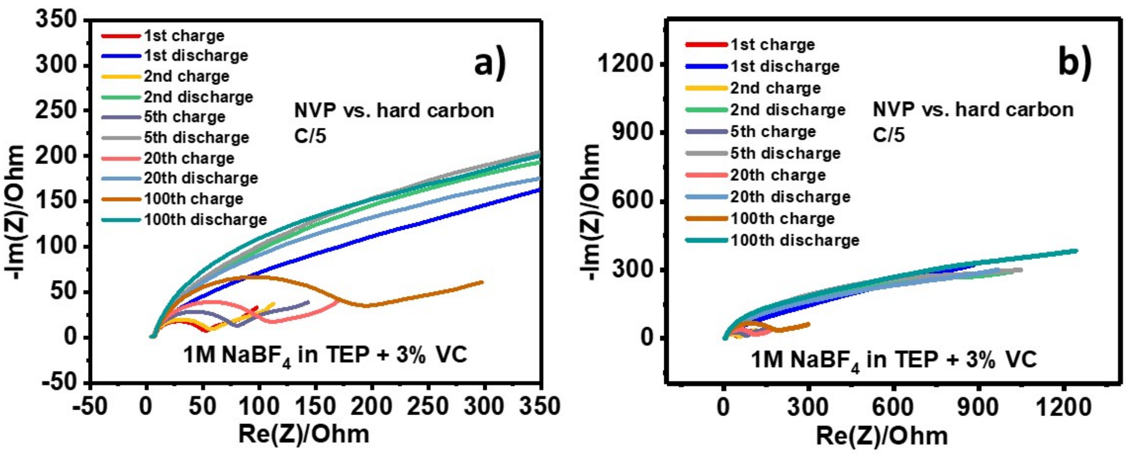

Fig. S3. Nyquist plots of NVP vs. hard carbon full-cell after 1st, 2nd, 5th, 20th, and 100th charge and discharge with 1M $NaBF_4$ in TEP with 3% VC (a) zoom-in and (b) zoom-out.

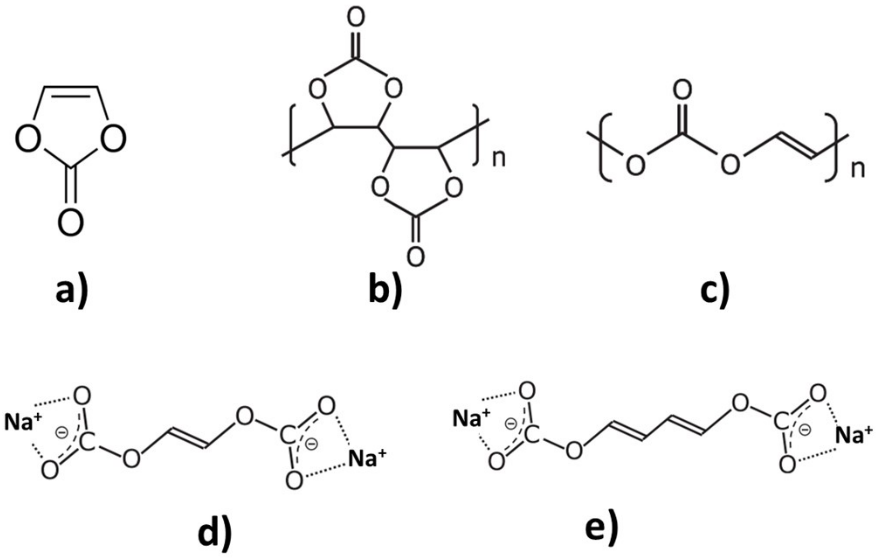

Fig. S4. Structure of (a) VC and possible decomposition product of VC: (b) radical polymer VC, (c) linear polymer VC, (d) sodium vinylene dicarbonate (SVD), and (e) sodium divinylene dicarbonate (SDVD).