

## Supplementary Information

### Synergy or interference? The effect of electrolyte additives and formation protocols combined in sodium-ion batteries

Katja Lahtinen<sup>a\*</sup>, Paul Latis<sup>a</sup>, Lucas Bruylands<sup>a</sup>, Guiomar Hernández<sup>a\*</sup>

<sup>a</sup> Department of Chemistry — Ångström Laboratory, Uppsala University, Box 538, SE-751 21 Uppsala, Sweden

\* Corresponding authors: [katja.lahtinen@kemi.uu.se](mailto:katja.lahtinen@kemi.uu.se), [guiomar.hernandez@kemi.uu.se](mailto:guiomar.hernandez@kemi.uu.se)

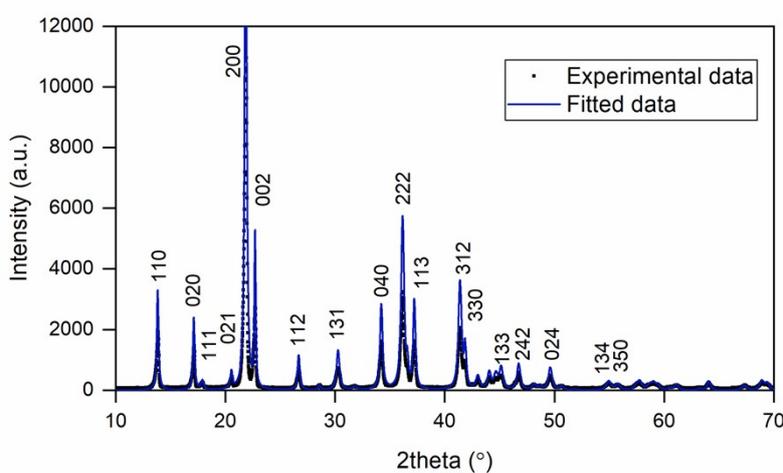


Figure S1. X-ray diffraction pattern of the synthesized NaBOB.

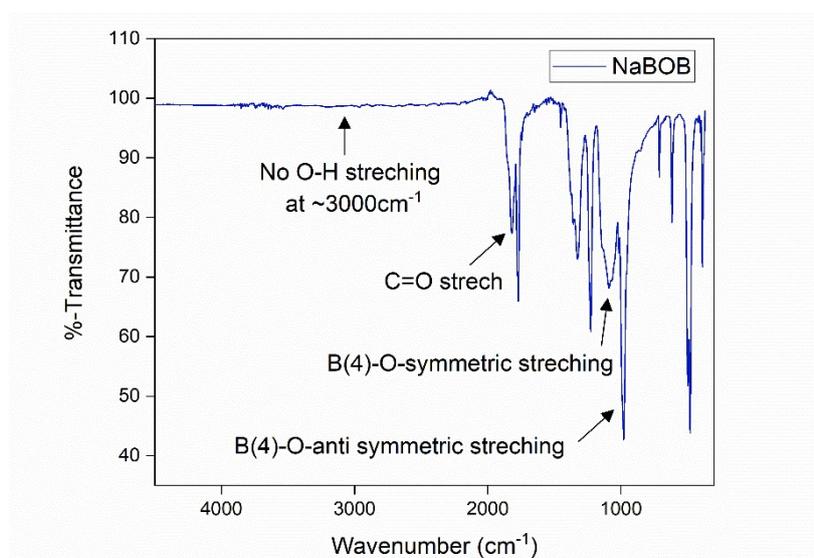


Figure S2. Fourier-transform Infrared spectroscopy data of the synthesized NaBOB.

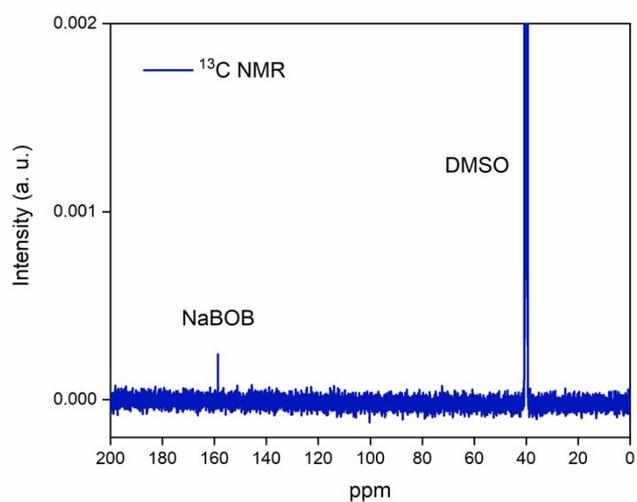


Figure S3.  $^{13}\text{C}$  NMR data of the synthesized NaBOB salt.

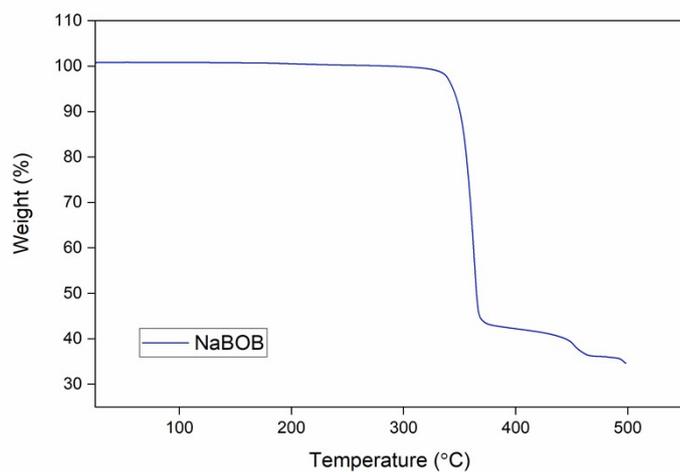


Figure S4. Thermogravimetric analysis of the synthesized NaBOB.

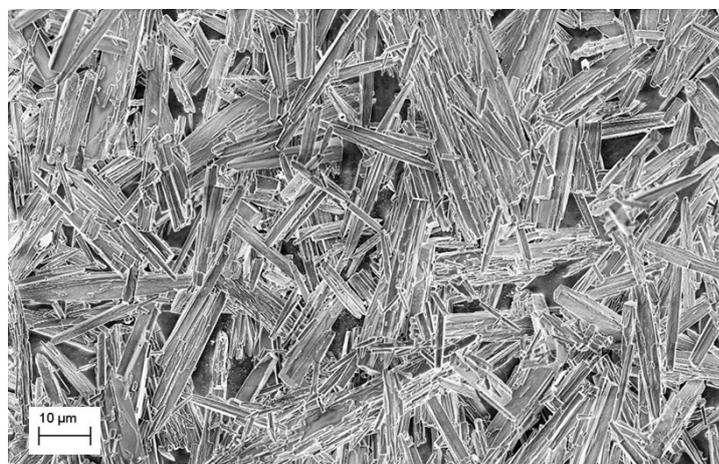


Figure S5. SEM image of the synthesized NaBOB crystals.

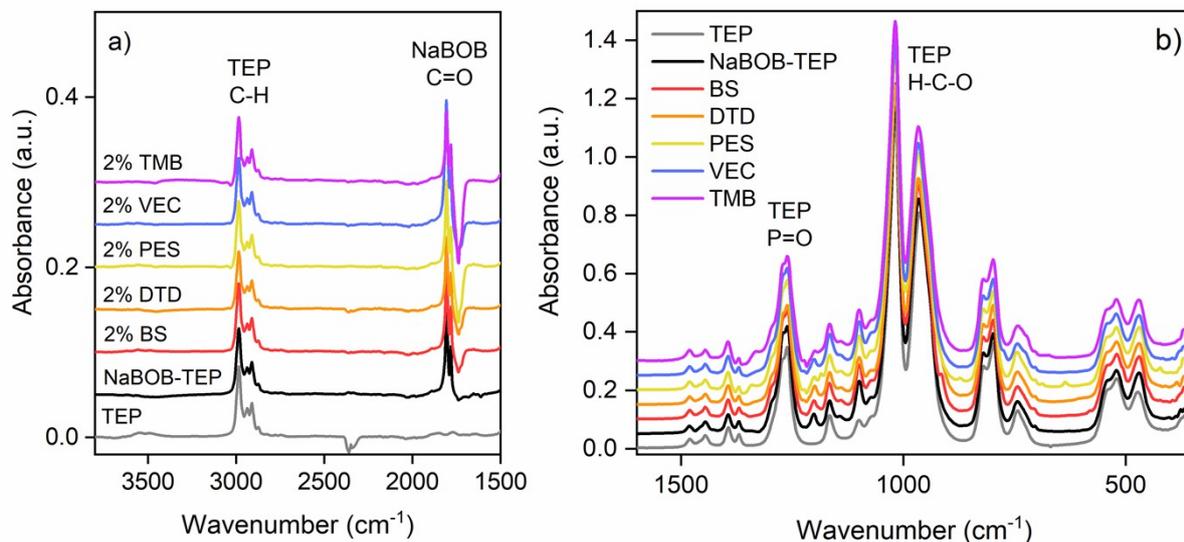


Figure S6. The FTIR spectra of the electrolytes containing 2 wt% of additives compared to the baseline 0.35 M NaBOB-TEP and pure TEP. The spectra are divided into two graphs to ease the readability of the plots. a) 3800–1500  $\text{cm}^{-1}$ , and b) 1550–350  $\text{cm}^{-1}$ .

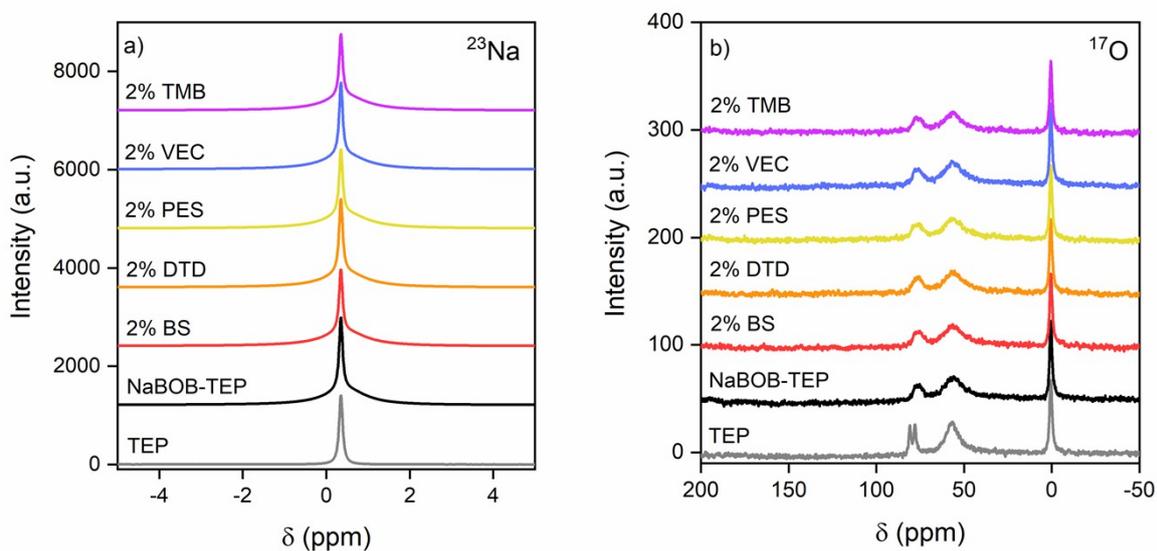


Figure S7. The a)  $^{23}\text{Na}$  NMR and b)  $^{17}\text{O}$  NMR spectra of the electrolytes containing 2 wt% of additives compared to the baseline 0.35 M NaBOB-TEP and pure TEP. Note that the TEP sample contains a  $\text{Na}^+$  signal from the NaCl reference tube. In the other samples the NaBOB  $\text{Na}^+$  peak is observed as a wide peak overlapping with the NaCl peak.

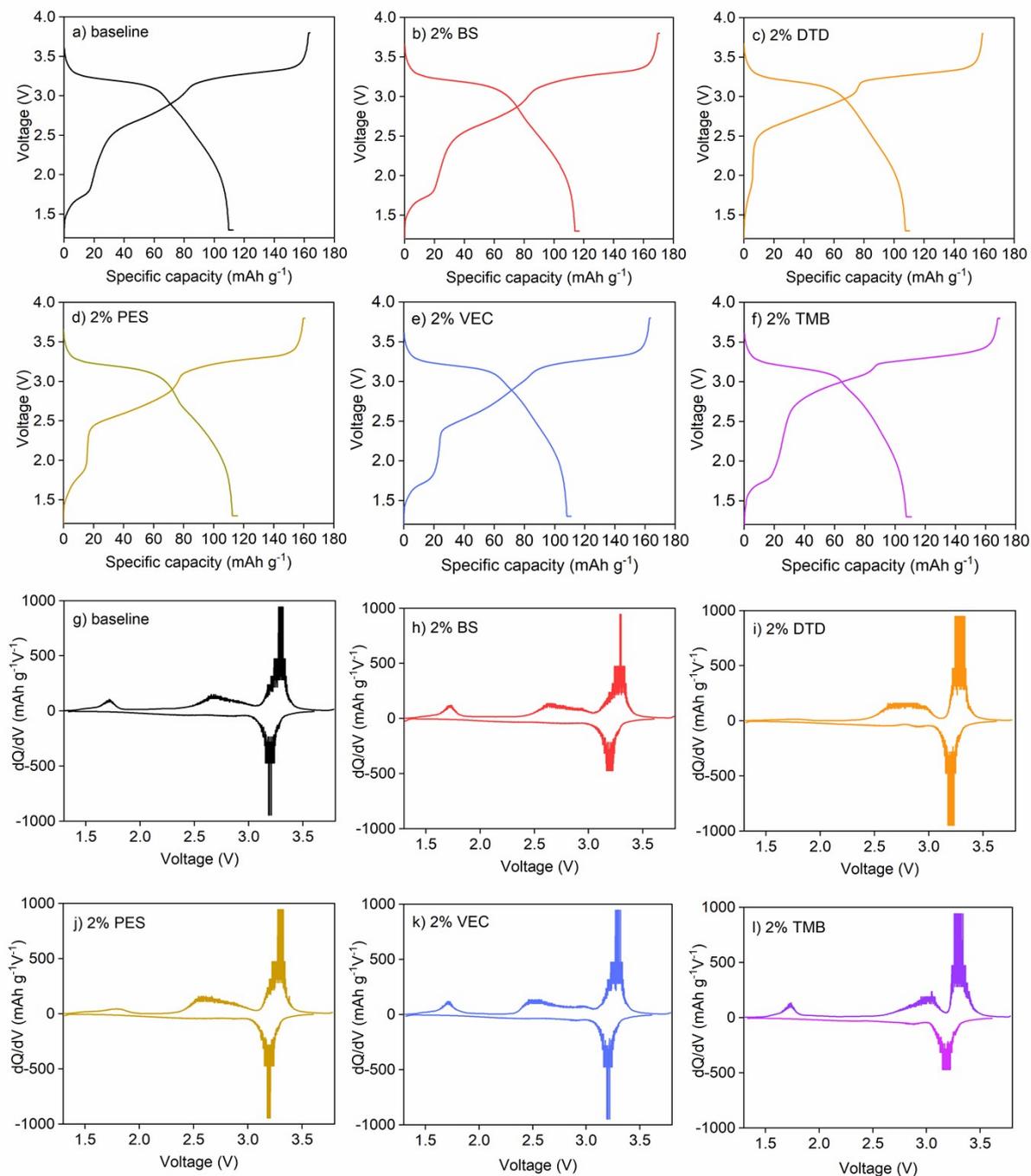


Figure S8. The first cycle charge-discharge voltage curves for the Normal formation protocol. a) the baseline, b) BS, c) DTD, d) PES, e) VEC, and f) TMB. The  $dQ/dV$  plots corresponding to the charge-discharge voltage curves for g) the baseline, h) BS, i) DTD, j) PES, k) VEC, and l) TMB.

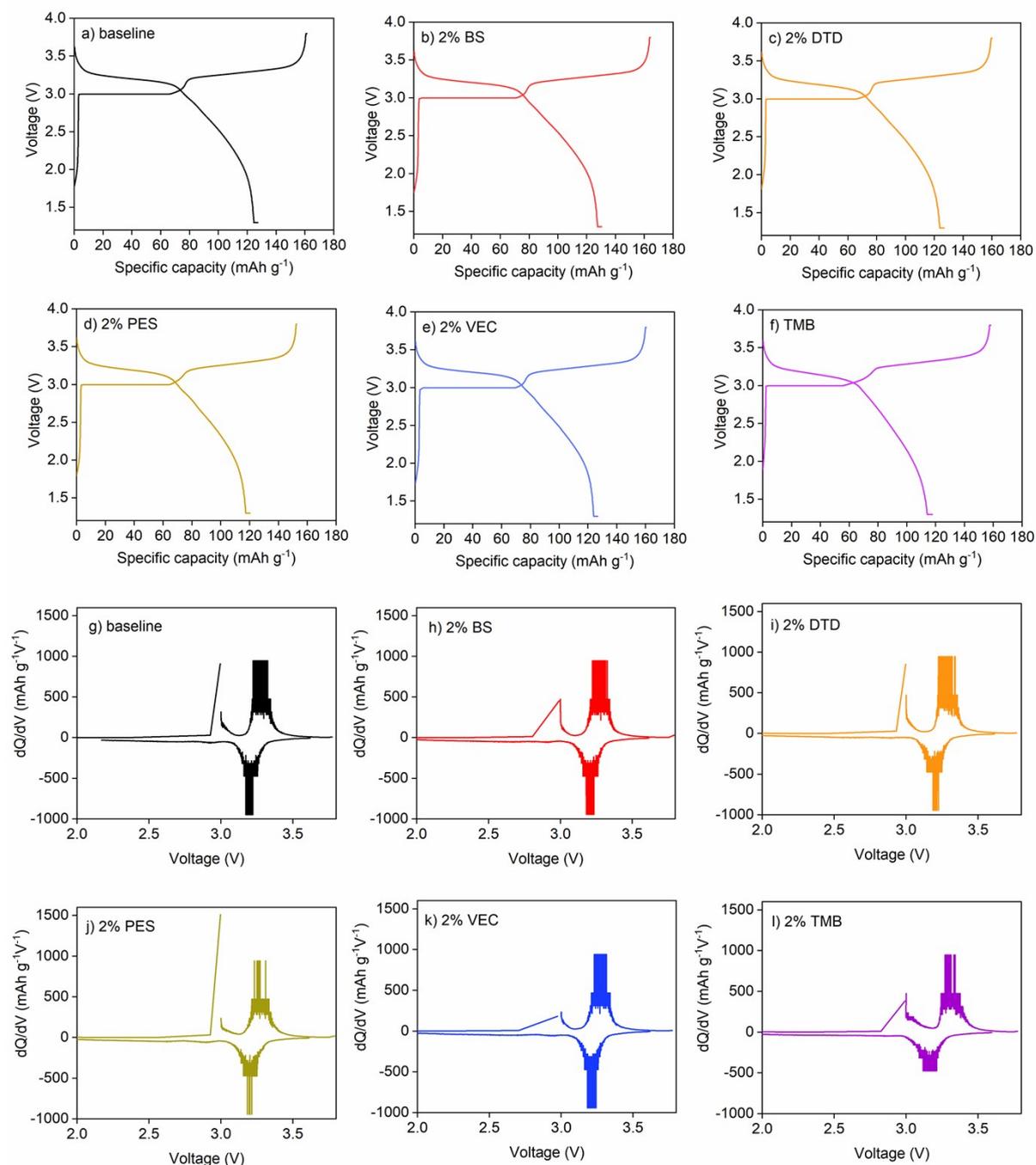


Figure S9. The first cycle charge-discharge voltage curves for the Skip formation protocol. a) the baseline, b) BS, c) DTD, d) PES, e) VEC, and f) TMB. The  $dQ/dV$  plots corresponding to the charge-discharge voltage curves for g) the baseline, h) BS, i) DTD, j) PES, k) VEC, and l) TMB.

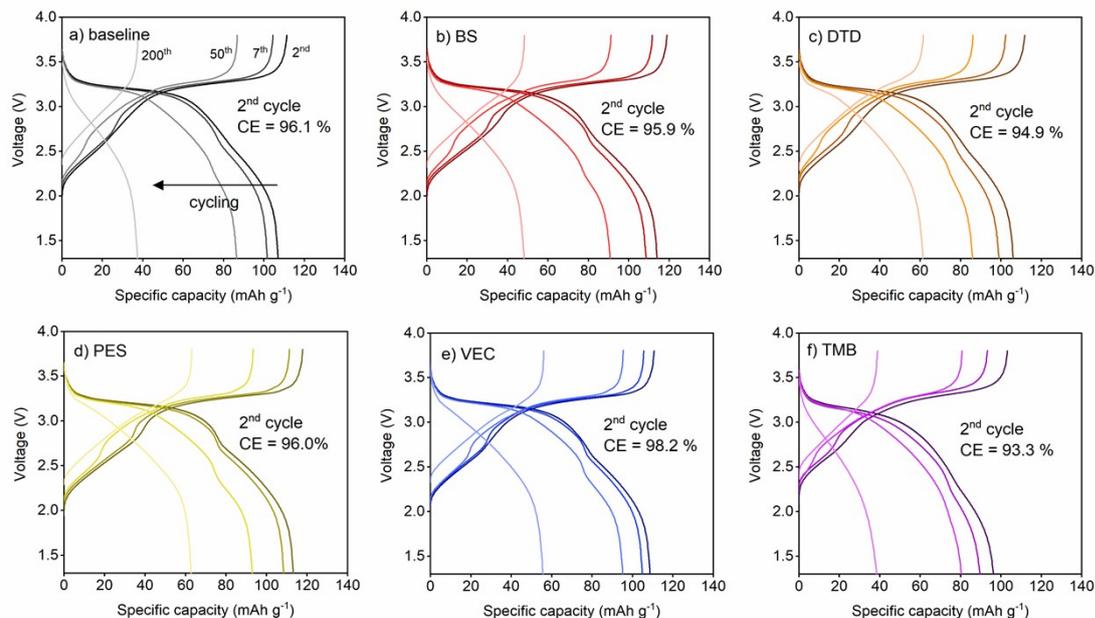


Figure S10. The 2<sup>nd</sup>, 7<sup>th</sup>, 50<sup>th</sup> and 200<sup>th</sup> cycle charge-discharge voltage curves after the Normal formation protocol. The 7<sup>th</sup> cycle equals to the first cycle cycled with 0.2 C. a) the baseline, b) BS, c) DTD, d) PES, e) VEC, and f) TMB.

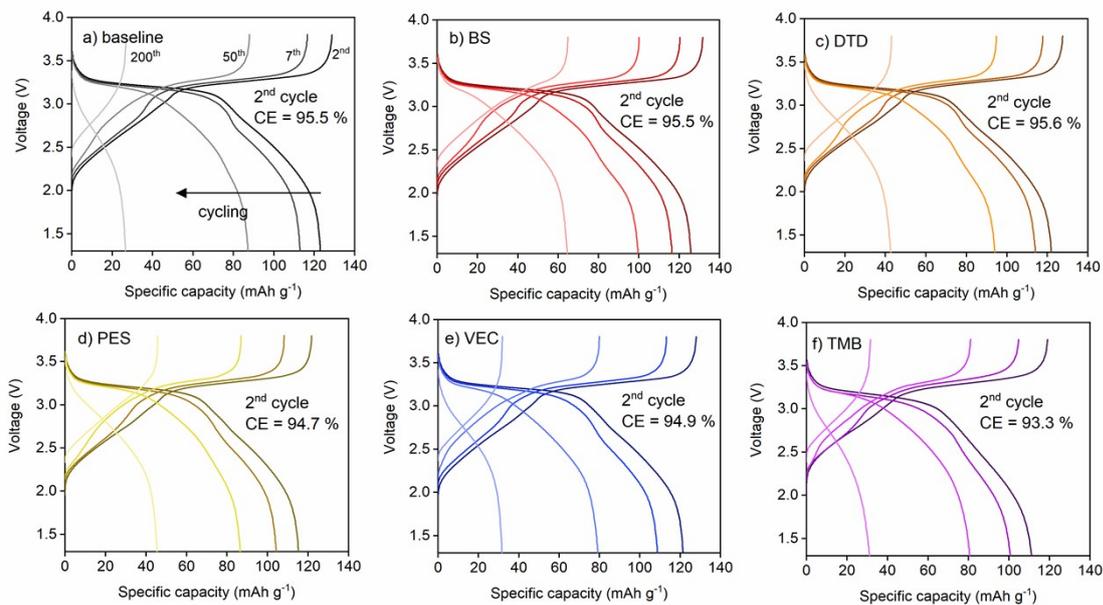


Figure S11. The 2<sup>nd</sup>, 7<sup>th</sup>, 50<sup>th</sup> and 200<sup>th</sup> cycle charge-discharge voltage curves after the Skip protocol. The 7<sup>th</sup> cycle equals to the first cycle cycled with 0.2 C. a) the baseline, b) BS, c) DTD, d) PES, e) VEC, and f) TMB.

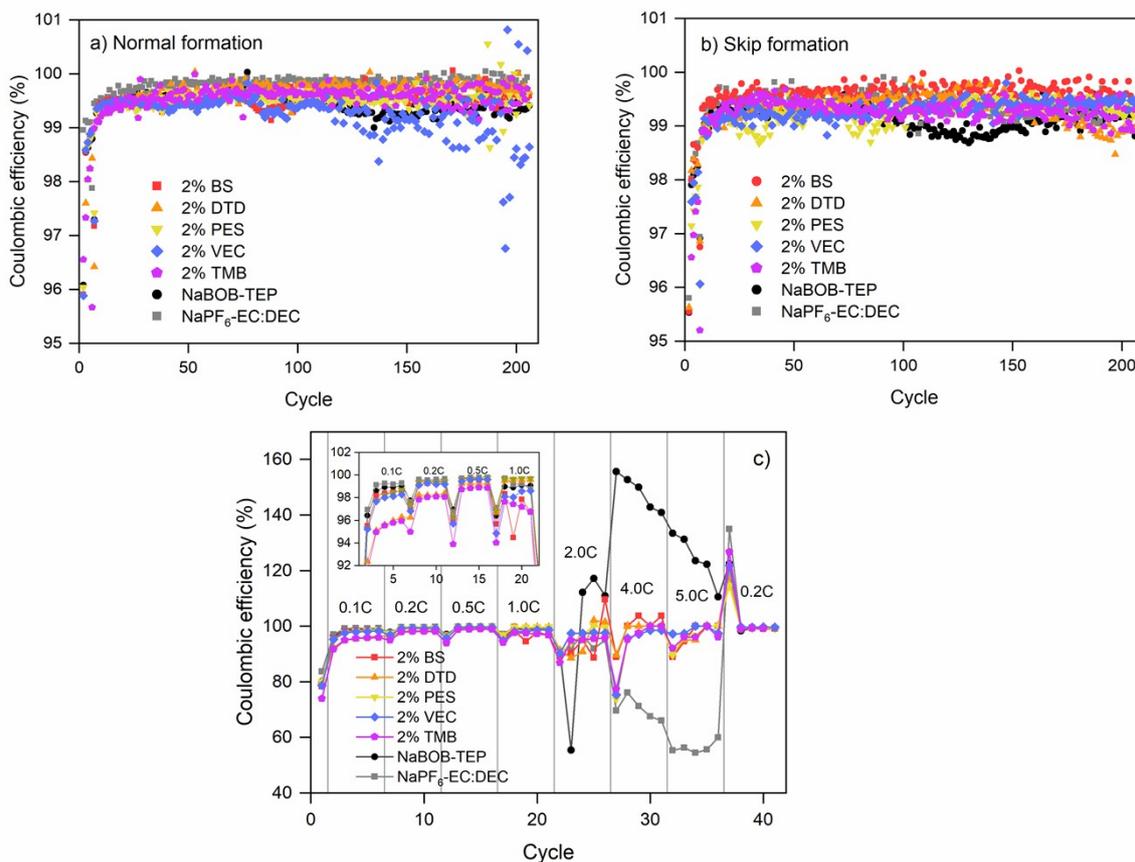


Figure S12. The Coulombic efficiencies during the a) cycling after Normal formation, b) cycling after Skip formation, and c) rate capability test.

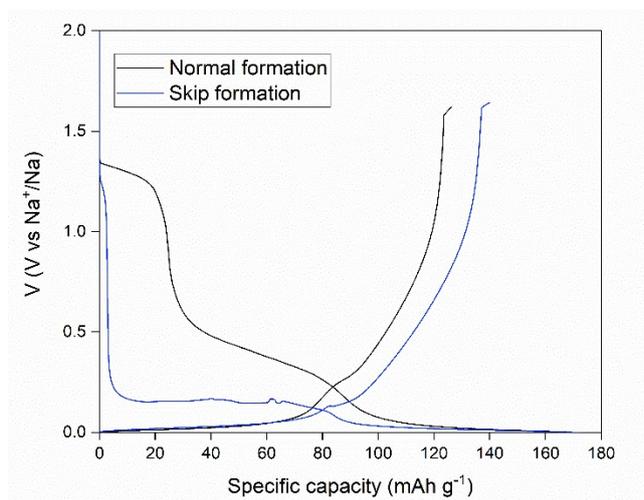


Figure S13. HC electrode potential during the PW-HC full cell formation with the Normal and Skip protocols using the baseline electrolyte. The reference electrode used in the measurement was partly desodiated PW.

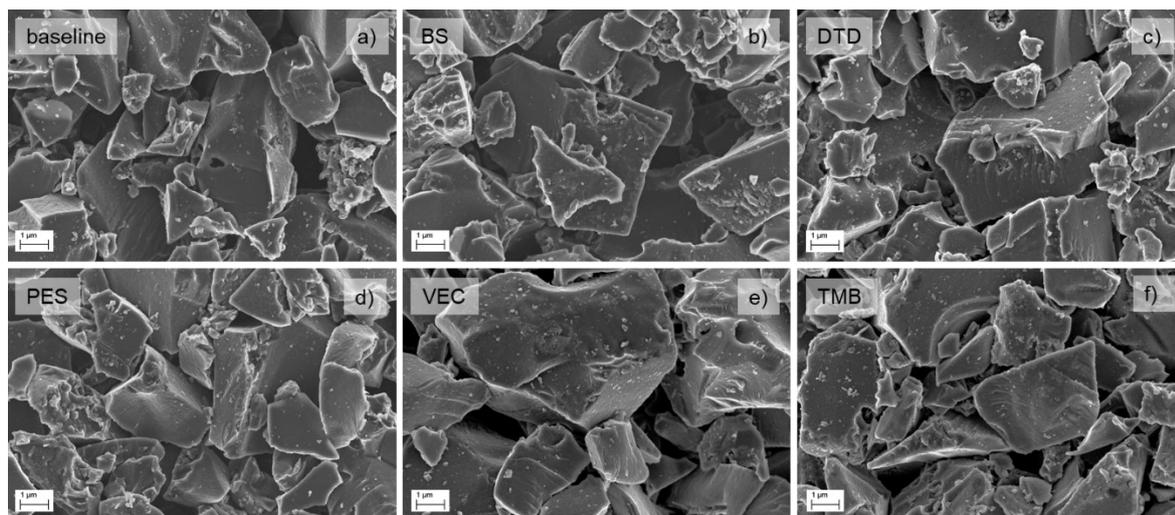


Figure S14. HC electrodes soaked in the NaBOB-TEP electrolytes. a) baseline, b) BS, c) DTD, d) PES, e) VEC, f) TMB.

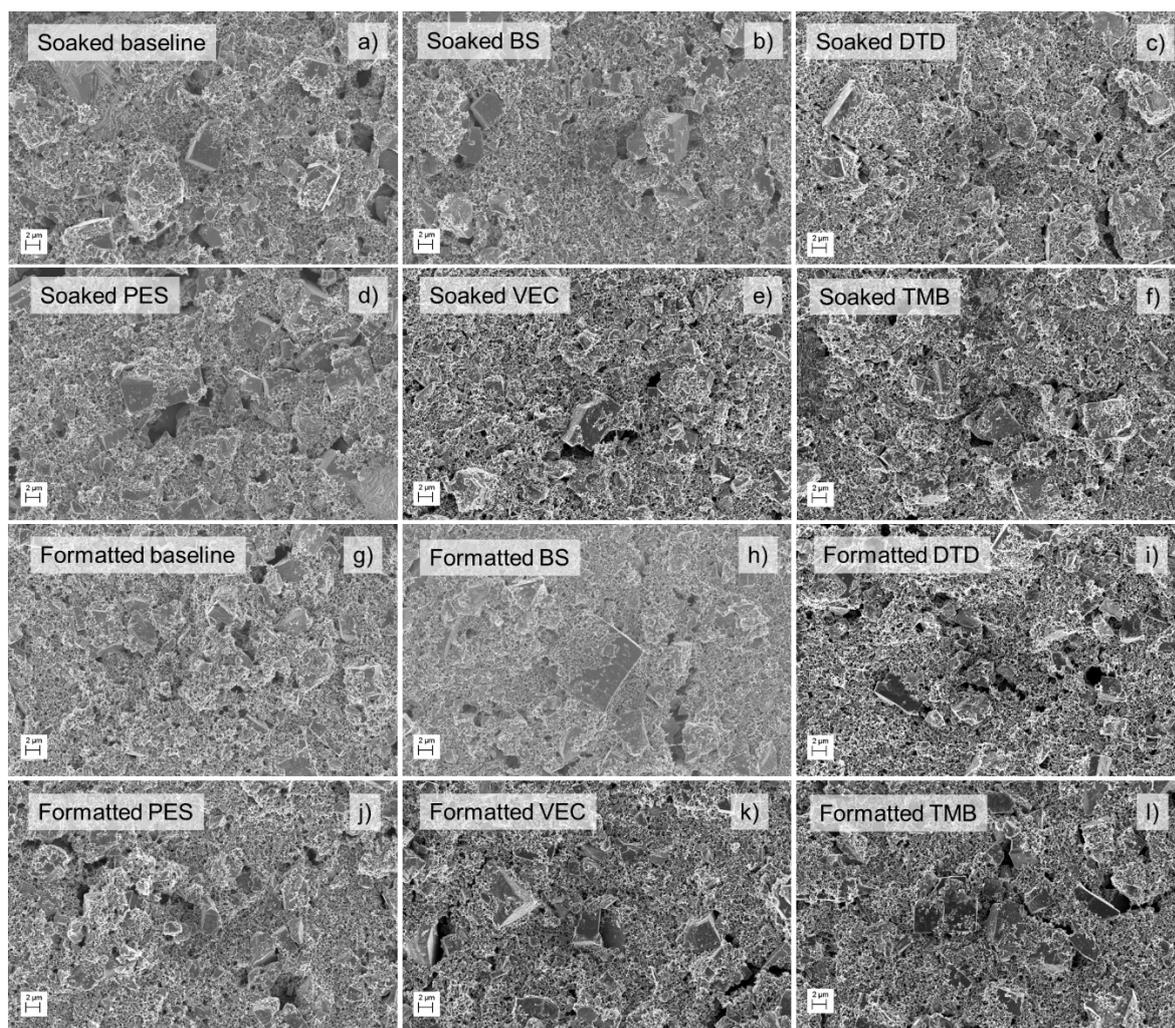


Figure S15. Prussian white electrodes soaked and after formation cycle in different additive containing 0.35 M NaBOB-TEP electrolytes. Soaked: a) baseline, b) BS, c) DTD, d) PES, e) VEC, f) TMB. Formatted: g) baseline, h) BS, i) DTD, j) PES, k) VEC, and l) TMB.

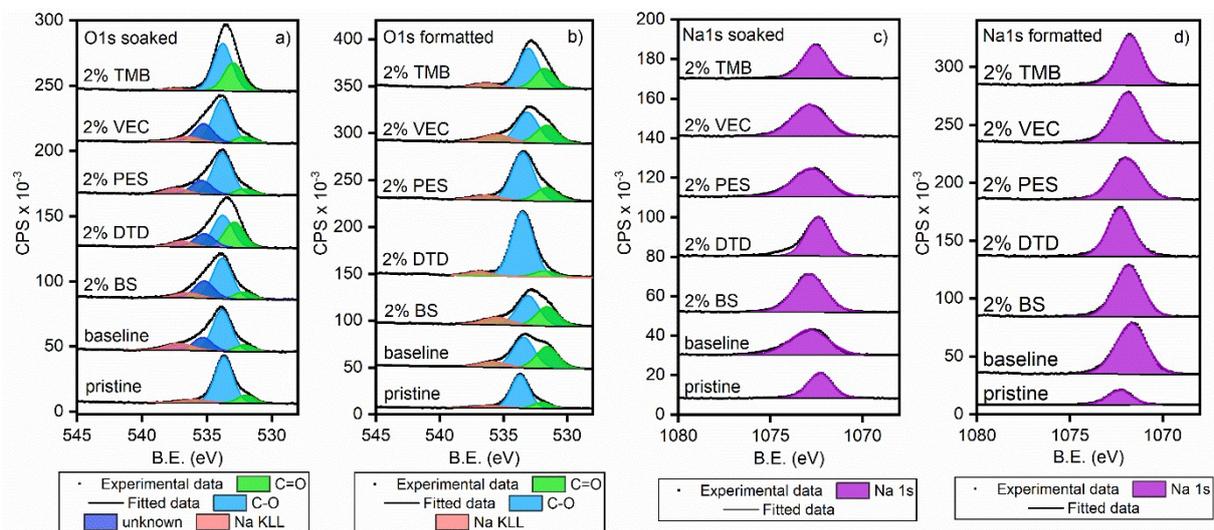


Figure S16. XPS spectra of the HC electrodes. a) O1s soaked, b) O1s formatted, c) Na1s soaked and d) Na1s formatted.

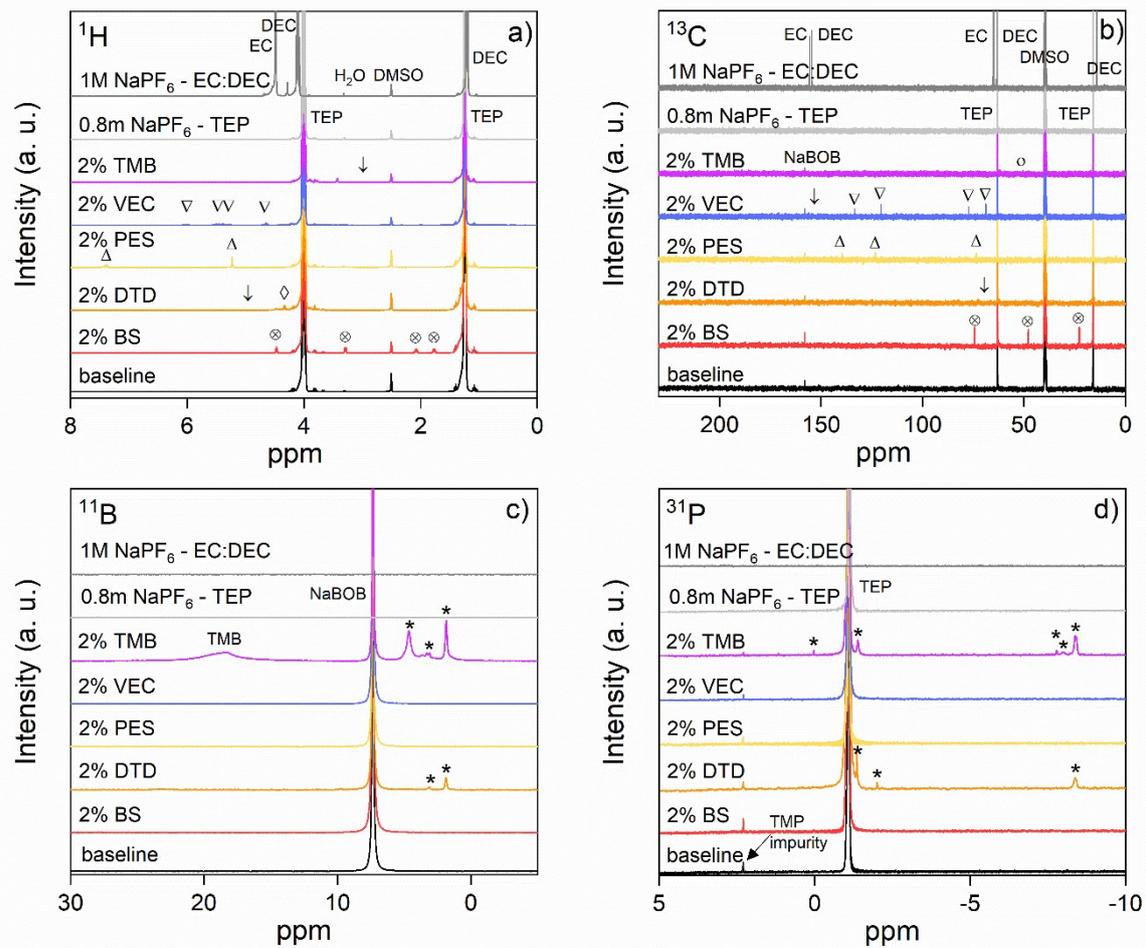


Figure S17. NMR spectra of the electrolytes stored at room temperature for 6 weeks.  $\downarrow$  marks a missing peak from an additive and  $*$  a new peak. The rest of the symbols are additive specific. a)  $^1\text{H}$ , b)  $^{13}\text{C}$ , c)  $^{11}\text{B}$  and d)  $^{31}\text{P}$ .

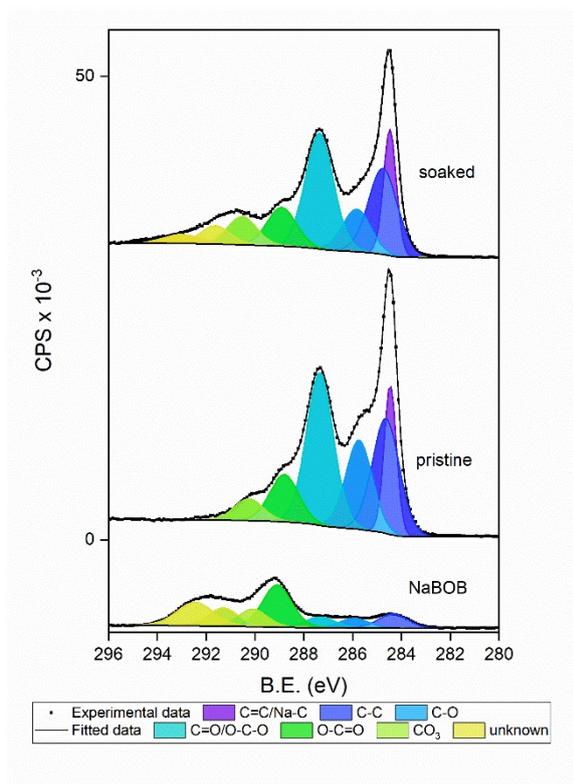


Figure S18. C1s XPS spectra of the pristine and 0.35 M NaBOB-TEP soaked Hard carbon electrodes compared to the C1s spectrum of NaBOB salt.