Sodium Bis(oxalato)borate (NaBOB) in Trimethyl Phosphate: A Fire-Extinguishing, Fluorine-Free, and Low-Cost Electrolyte for Full-Cell Sodium-Ion Batteries

Ronnie Mogensen, Simon Colbin, Ashok Menon, Erik Björklund, Reza Younesi

Submitted date: 10/03/2020 • Posted date: 11/03/2020
Licence: CC BY-NC-ND 4.0

Citation information: Mogensen, Ronnie; Colbin, Simon; Menon, Ashok; Björklund, Erik; Younesi, Reza (2020): Sodium Bis(oxalato)borate (NaBOB) in Trimethyl Phosphate: A Fire-Extinguishing, Fluorine-Free, and Low-Cost Electrolyte for Full-Cell Sodium-Ion Batteries. ChemRxiv. Preprint. https://doi.org/10.26434/chemrxiv.11962524.v1

Sodium-ion batteries based on all-naturally-abundant elements, in which no cobalt, nickel, copper, and fluorine is used, can lead to a major breakthrough in making batteries more sustainable. Safety aspects - in particular flammability of electrolytes - in the state-of-the-art battery technology is another important concern, especially for applications in which large numbers of cells are employed. Non-flammable battery electrolytes studied so far are based on highly fluorinated compounds or high salt concentrations, which suffer from high cost and toxicity. We here propose an electrolyte based on a single solvent and lowcost and fluorine-free salt at the lower range of “standard” concentrations. Our results show - for the first time - that sodium bis(oxalato)borate (NaBOB) is soluble in the nonflammable solvent trimethyl phosphate (TMP). This finding enables a non-flammable electrolyte with high ionic conductivity and promising electrochemical performance in fullcell sodium-ion batteries. An electrolyte of 0.5 M NaBOB in TMP provides ionic conductivity of 5 mS cm⁻¹ at room temperature, which is comparable to commonly used electrolytes based on sodium hexafluorophosphate (NaPF₆) and organic carbonate solvents. The proposed electrolyte shows the Coulombic efficiency of above 80% in the first cycle, which increased to about 97% from the second cycle in sodium-ion battery fullcells consisting of a hard carbon anode and Prussian white cathode. This work opens up new opportunities to design safe electrolytes which can further be optimized with electrolyte additives such as vinylene carbonate for industrial applications.
| Filename          | Size          | Link                        |
|-------------------|---------------|-----------------------------|
| TMP 0.5M NaBOB.mp4 | 88.48 MiB     | view on ChemRxiv - download file |
| TMP 0.4M NaBOB.mp4 | 55.96 MiB     | view on ChemRxiv - download file |
| TMP 0.3M NaBOB.mp4 | 62.90 MiB     | view on ChemRxiv - download file |
| TMP 0.2M NaBOB.mp4 | 59.83 MiB     | view on ChemRxiv - download file |
| TMP 0.1M NaBOB.mp4 | 61.47 MiB     | view on ChemRxiv - download file |
| TMP.mp4           | 57.49 MiB     | view on ChemRxiv - download file |
Sodium bis(oxalato)borate (NaBOB) in trimethyl phosphate: a fire-extinguishing, fluorine-free, and low-cost electrolyte for full-cell sodium-ion batteries

Ronnie Mogensen1, Simon Colbin1, Ashok Sreekumar Menon1, Erik Björklund1, Reza Younesi1

1 Department of Chemistry-Ångström Laboratory, Uppsala University, Box 538, SE-75121 Uppsala, Sweden

Sodium-ion batteries based on all-naturally-abundant elements, in which no cobalt, nickel, copper, and fluorine is used, can lead to a major breakthrough in making batteries more sustainable. Safety aspects in particular flammability of electrolytes in the state-of-the-art battery technology is another important concern, especially for applications in which large numbers of cells are employed. Non-flammable battery electrolytes studied so far are based on highly fluorinated compounds or high salt concentrations, which suffer from high cost and toxicity. We here propose an electrolyte based on a single solvent and low-cost and fluorine-free salt at the lower range of "standard" concentrations. Our results show for the first time that sodium bis(oxalato)borate (NaBOB) is soluble in the non-flammable solvent trimethyl phosphate (TMP). This finding enables a non-flammable electrolyte with high ionic conductivity and promising electrochemical performance in full-cell sodium-ion batteries. An electrolyte of 0.5 M NaBOB in TMP provides ionic conductivity of 5 mS cm⁻¹ at room temperature, which is comparable to commonly used electrolytes based on sodium hexafluorophosphate (NaPF₆) and organic carbonate solvents. The proposed electrolyte shows the Coulombic efficiency of above 80% in the first cycle, which increased to about 97% from the second cycle in sodium-ion battery full-cells consisting of a hard carbon anode and Prussian white cathode. This work opens up new opportunities to design safe electrolytes which can further be optimized with electrolyte additives such as vinylene carbonate for industrial applications.

Sodium-ion batteries have been proposed to provide a more sustainable battery system compared to lithium-ion battery technology, facilitating use of rechargeable high energy density batteries for large scale applications such stationary storage.¹⁻⁴ This is particularly achievable if cells contain only naturally abundant elements and by eliminating, among others, cobalt, nickel and copper. Safety is another important concern for large scale applications, and in this respect the flammability of the non-aqueous electrolytes may limit use of the state-of-the-art battery technology in some applications.⁵,⁶

Most electrolytes used for sodium-ion batteries today are based on the same formula as the lithium-ion counterparts using organic carbonate solvents.⁷ It should also be noted that the electrolyte composition is a concern for sustainability since the electrolytes used in both sodium- and lithium-ion batteries employ fluorinated salts such as sodium
hexafluorophosphate (NaPF₆) and sodium bis(trifluoromethanesulfonyl)imide (NaTFSI) which are toxic and expensive to produce.³,⁸

Here, we address both issues of the sustainability and safety of modern batteries by presenting a fluorine-free and non-flammable electrolyte for use in sodium-ion batteries. The proposed electrolyte is based on sodium bis(oxalato)borate (NaBOB) salt and trimethyl phosphate (TMP) as the sole solvent. Since its synthesis and characterization by W. Xu and C. Angell, LiBOB has been used with great success in lithium-ion batteries, both as a stand-alone salt¹⁰–¹⁵ and additive¹⁶–¹⁸. NaBOB however, first synthesized by Zavalij et al.¹⁹ in 2003 has been considered too insoluble in organic solvents to be used in practice. Thus, salts like sodium-difluoro(oxalato)borate (NaDFOB)²⁰ as well as other functionalized versions of NaBOB²¹ have been developed to address this. In this work, we show the first example of a suitably conductive NaBOB-based electrolyte cycled in full cell sodium-ion batteries with hard carbon anodes and Prussian white cathodes. The results are compared with NaPF₆ in TMP electrolytes with and without additives.

TMP has previously been shown to reduce the flammability of electrolytes and therefore been used as co-solvent together with flammable solvents like ethylene carbonate (EC) and propylene carbonate (PC).²²–²⁵. TMP as a sole solvent suffers the major shortcoming of poor electrochemical stability, especially when using hard carbon anodes for sodium²⁴ or graphite anodes for lithium²⁶,²⁷ due to insufficient anode passivation. This problem has been overcome by using highly concentrated electrolytes based on NaN(SO₂F)₂ (NaFSI), LiN(SO₂F)₂ (LiFSI) and LiN(SO₂C₂F₅)₂ (LiBETI) salts in studies by other authors.²⁶–²⁹ While highly concentrated electrolytes can combine good cyclability and safety, they do have some detrimental attributes like low ionic conductivities, high viscosity, and furthermore, high cost due to the large quantity of fluorinated salts.

Here, we for the first time show that the combination of relatively low concentration of NaBOB salt (0.5 M) with TMP provides remarkably stable cycling, demonstrating a very promising low-cost and green battery chemistry.

Results and Discussion

“Structure, conductivity and flammability” or “Properties of NaBOB”

The synthesis and structural properties of NaBOB has previously been investigated by Zavalij et al.¹⁹ and their work provided a good foundation for the synthesis and determination of the purity of the NaBOB prepared in this work. LiBOB performance is sensitive to impurities¹⁷ and therefore the NaBOB used in this work was recrystallized in TMP. Figure 1 shows X-ray diffraction, elemental analysis and TGA of NaBOB salt synthesized in this work. The combined results from XRD and elemental analysis based on combustion analysis and ICP-OES show that the salt has a high purity as evidenced by the stoichiometry and no detectible impurity phases in the diffractogram (see tables S1 supplemental for XRD analysis details). The TGA results indicate that NaBOB salt is stable up to 300°C in nitrogen, which is an important advantage compared to NaPF₆ being stable up to 140 °C under vacuum.³⁰
Figure 1. TGA results showing thermal stability of NaBOB in nitrogen gas at 5 °C min⁻¹ heating rate (a) and Rietveld refinement of NaBOB powder X-ray diffraction data (b). The results from the ICP-OES & combustion analysis of the NaBOB powder used for the electrolytes (c).

Figure 2 shows that the ionic conductivity of NaBOB-TMP increases with NaBOB concentration, ultimately reaching a 5 mS cm⁻¹ for the 0.5 M NaBOB in TMP electrolyte at room temperature, which is similar to a corresponding ionic conductivity of 6 mS cm⁻¹ for 1 M NaPF₆ in TMP. These values are within the range of ionic conductivity of practical non-aqueous electrolytes based on carbonates. The maximum concentration of NaBOB in TMP, i.e. 0.5 M, was achieved as a clear solution after both heating and rigorous stirring while a 0.6 M sample remained turbid after an identical treatment. This lower concentration of 0.5 M NaBOB compared to conventional electrolytes based on 1 M NaPF₆ is in favour of reducing the electrolyte cost. In addition, the raw materials used for synthesis of NaBOB has are very common and benign compared to raw materials used in production of the PF₆⁻ salts such as HF, PCl₅ and fluorine gas. Furthermore, the synthesis procedure for NaBOB is facile, safe and does not require an inert environment.

Flammability tests were performed using a butane lighter in order to verify that the addition of NaBOB does not change the flammability properties of the TMP solvent. TMP did not ignite for any concentration of NaBOB (see videos in Supplemental Information) while a reference
sample consisting of PC showed a strong self-propagating flame. Immediately upon removal of the flame source from the NaBOB-TMP samples, all traces of fire disappeared, thus making it impossible to determine a self-extinguishing time. In contrast, propylene carbonate burnt vigorously until entirely consumed using the same experimental setup (see figure 3).

Figure 3. Flammability tests for TMP 0.5M NaBOB (left) and Propylene carbonate (right). “T” indicates time in seconds passed between frames.

“Electrochemical performance”

Cyclic voltammetry experiments in figure 4 a show that the NaBOB undergoes reduction starting at 1.6 V vs. Na⁺/Na in the first scan. However, as cycling progresses, effective passivation becomes evident as the reduction current significantly decreases. CV also shows oxidation current at 3 V in the first scan which can be decomposition of some reduction product during the first cycle. The stability however extends to approximately 4 V after the first cycle. Figure 4b displays CV of 1 M NaPF₆ in TMP, where the reduction starts at 1 V in the first sweep, which is shifted to slightly lower voltages in subsequent sweeps (see figure 4b, insert). The reduction current however increases in the following sweeps which suggest formation of a poor passivation layer in 1 M NaPF₆ in TMP electrolyte.

Figure 4. Cyclic voltammetry for 0.5 M NaBOB performed using a PW reference electrode (a) and 1 M NaPF₆ using a sodium-metal counter electrode (b). Scan speed was set to 1 mV s⁻¹ for both cells.
The 0.5 M NaBOB in TMP electrolyte was further evaluated in two-electrode sodium-ion full cells consisting of a hard carbon anode and a Prussian white cathode. The results in figure 5a and 5b show that the NaBOB-TMP electrolyte provides superior cycling performance compared to the NaPF6-TMP electrolyte with Coulombic efficiency (CE) at 75% compared to that of 55% for NaPF6 for the first cycle. The additive-free NaBOB-TMP electrolyte enables stable cycling while the additive free NaPF6-TMP, in accordance with literature, has very poor performance and only maintains 31 mAh g⁻¹ at the 10th cycle compared to the 108 mAh g⁻¹ of NaBOB-TMP. The SEI formation in the NaBOB-based electrolyte was observed between 1.5-2.5 V during the first charge and the early NaBOB decomposition into carbonates stabilize the TMP solvent while NaPF6 clearly suffers from suboptimal passivation.

Figure 5c and 5d display voltage profile of hard carbon anode and Prussian white cathode individually versus the reference electrode in a three-electrode cell. The reference electrode was Prussian white as an alternative to unreliable Na metal electrode (note that hard carbon half-cells became unstable when using sodium metal counter electrodes which yielded no useful data. The PW half-cells using NaBOB-TMP suffered from high initial polarization while NaPF6-TMP suffered from rapid capacity fading which are likely due to parasitic reactions on Na metal, see Figure S1 for half-cell data). During the first charge the reduction of NaBOB is clearly seen as a distinct plateau in the hard carbon potential during the initial stages (figure 5c) that is absent from the NaPF6 counterpart (figure 5d). These results are in agreement with CV data presented in Figure 4 indicating active contribution of NaBOB in formation of SEI on hard carbon, and it is in agreement with previous studied on LiBOB showing relatively high onset reduction potential for LiBOB.

![Figure 5](image-url)

**Figure 5.** Galvanostatic cycling. 1st, 5th, and 10th charge-discharge curves in sodium-ion full-cells based on hard carbon anode and Prussian white cathode using 0.5 M NaBOB in TMP electrolyte (a) and 1 M NaPF6 in TMP electrolyte (b). The first charge from three electrode cells using 0.5 M NaBOB in TMP(c) and 1 M NaPF6 in TMP electrolyte (d).
XPS measurements were performed on hard carbon anodes after one full cycle in full-cells to compare the composition of SEI in the aforementioned electrolytes. Figure 6 displays the XPS spectra with peak assignments representing species present in the SEI on hard carbon and the relative atomic concentration. The C1s spectrum of the pristine hard carbon sample contains two major peaks at 284.5 eV and 287 eV representing hard carbon and NaCMC binder. The C-C peak of hard carbon particles becomes almost invisible in the cycled electrodes, which indicates SEI formed on hard carbon is thicker than ~10 nm (probing depth of in-house XPS with Al kα source). The C 1s and O 1s spectra of cycled electrodes reveal that the composition of SEI differs with the chemistry of electrolyte; the SEI in the cell with NaBOB-TMP possesses hydrocarbon, C-O, and -CO3 species while being rich with C=O and/or O-C-O.36 However, the SEI in the cell with NaPF6-TMP contains more C-O and P-O species. The C1s spectrum of the cell with NaPF6-TMP also shows a small peak at the binding energy of ~283 eV indicating residual intercalated Na ions remained into the hard carbon framework even after full charge.37 This peak is absent in the cell with NaBOB-TMP suggesting successful fully desodiation of hard carbon at the end of charge. The P 2p, F 1s, and B 1s spectra disclose that both NaBOB and NaPF6 salts as well as TMP solvent contributed to SEI formation. The strong fluorine signal from NaPF6-TMP in the F 1s spectra shows that a part of the phosphorus originates from NaPF6. However, TMP also participated in SEI formation as evidence from the peak at 532 eV in O 1s spectrum of NaPF6-TMP sample, which is assigned to C-O-P and P=O species since there is no carbonate formed according to C 1s spectrum.38 P 2p spectrum of hard carbon from the cell with NaBOB-TMP displays a small peak which is originated from TMP as there is no other source of phosphorus in this sample. All samples show one peak on Na 1s spectra, originated from NaCMC binder and Na-containing SEI species.

The electrochemical test and surface analysis presented above clearly shows the active role of NaBOB compared to NaPF6 in electrolytes based on TMP in formation SEI on hard carbon. However, despite demonstrating benefits over the NaPF6-based electrolyte, the additive-free NaBOB-TMP still suffers from capacity fading and a relatively low Coulombic efficiency of the first cycle (i.e. 75%) which needs to be improved. It has previously been shown that additives can be used to further improve first cycle Coulombic efficiency and cycling stability.39–41 So, in order to test if the passivation of hard carbon could be improved in either system we tested electrolytes containing both 5 and 10 vol % vinylene carbonate (VC) in galvanostatic cycling (see figure 7).

The addition of 5 vol % VC to NaBOB-TMP electrolyte increases the Coulombic efficiency of the 1st cycle from 75% to 80% while the cells with higher additive amount of 10 vol % VC shows somewhat erratic behavior (Figure 7a). All our replicate cells showed good repeatability except the NaBOB 10 vol % VC cells that showed considerable variation, with 1st cycle Coulombic efficiency values varying between 62% and 82%, suggesting that this is a more sensitive system than the other compositions. Figure 7c shows that the decomposition plateau of NaBOB gradually disappears with increasing addition of VC, thus it appears that VC and NaBOB both participates in the SEI formation. The positive impact of VC becomes questionable at the higher 10 vol % VC loading, as sometimes a second feature close to 2.4 V appears which indicates excessive VC breakdown with detrimental effects on the cell reversibility.
Figure 6. XPS spectra and relative atomic concentration of elements present on the surface of pristine and cycled hard carbon anodes after one cycle in HC-FW full-cells using electrolytes of 0.5 M NaBOB in TMP or 1 M NaPF$_6$ in TMP.

VC is however essential for stability in NaPF$_6$-TMP electrolyte as the capacity fading is substantially suppressed in VC-containing cells in Figure 7b. The addition of VC to NaPF$_6$-TMP system leads to appearance of a new feature in the voltage curve at 1.6 V during charge (Figure 7d, insert). This feature looks quite similar for both 5 and 10 vol % albeit with a slightly quicker voltage increase for 10% VC. The effect of VC on the initial Coulombic
efficiencies is dramatic as the CE of 1st cycle increases from 56% without VC, to almost 84% for both electrolytes with 5% and 10 vol% VC. This indicates that the passivation of hard carbon anode occurs by means of VC rather than NaPF₆ or TMP. It also appears that the process is less sensitive to the concentration of VC than NaBOB-TMP as there is no evidence of excessive additive decomposition even at 10 vol% VC. All of the best performing cells using VC with either NaBOB or NaPF₆ display a rapid increase of the Coulombic efficiency and reach above 96.5% CE by the second cycle, as shown in Figure 7e. Note that the error bar disclose the variation in CE obtained from identical cells.

Figure 7. Galvanostatic cycling of sodium-ion full cells based on hard carbon anodes and Prussian white cathodes cycled with 0, 5, 10 vol% VC additive (a & b) with zoomed in view of the SEI forming region for 0.5 M NaBOB (c) and 1 M NaPF₆ (d). Cycling was performed between 3.8 and 1 V and two replicate cells are included for each electrolyte composition except NaBOB 10% VC that has three replicates. Coulombic efficiency of the first five cycles for 0.5 M NaBOB and 1 M NaPF₆ (e). Coulombic efficiencies are averaged from the replicate cells with the standard deviation denoted by the error bars.
Extended cycling for all compositions was performed up to cycle 50. However, the capacity for the cells with 1 M NaPF$_6$ in TMP without VC additive fades rapidly due the unstable cycling and thus these results are omitted. Both 5 & 10 vol % VC containing 1 M NaPF$_6$ in TMP cells yield impressive cycling compared to their additive free analogue (Figure 8a), confirming that VC continues to protects TMP against the hard carbon surface over time.

As cycling progresses it appears that the long-term performance in the 0.5 M NaBOB electrolytes also gains a long-term performance boost by addition of VC, even if the improvement is not as dramatic as for NaPF$_6$. Based on the results, a VC-based or at least a VC containing passivation layer is preferable to the SEI formed by NaBOB alone as the 0.5 M NaBOB cells using 5 vol % VC loading consistently show improved long-term capacity retention. It should be mentioned that the cell with 0.5 M NaBOB in TMP electrolyte with 10 vol % VC often showed worse performance than the baseline additive-free electrolyte even though only the best performing cell is shown in Figure 8 with very impressive results (see Figure S2 in supplemental information for the results from all cells). These cycling performance in full-cells is almost similar to our previous result on half-cells based Prussian white cathodes using 1.5 M NaPF$_6$ in dimethoxyethane.$^{42}$

NaBOB salt is without doubt superior NaPF$_6$ salt when used in TMP without additives, however when additive free NaBOB is compared to electrolytes that use VC, it is generally true that the additive free electrolyte loses more sodium inventory during the first cycle and suffers slightly lower Coulombic efficiency in later cycles (see Figure 8).

The best performing cells of both TMP-NaBOB and TMP-NaPF$_6$ using 5 & 10 vol % VC all have CE values between 98.5-99% after 10 cycles while additive free TMP-NaBOB cycles above 97.5% CE in cycles 4-50. Although longer cycling is required to reveal if the SEI is truly stable, the electrolytes tested here represent an important step towards practically viable non-flammable sodium-ion batteries.

Figure 8. Extended galvanostatic cycling at 30 mA g$^{-1}$. Results from the best performing cells of all replicates, showing specific discharge capacity based on cathode mass (a) and CE for the same cells (b).
Conclusion

The use of NaBOB as the electrolyte salt in sodium-ion batteries is for the first time shown here. A non-flammable and fluorine-free electrolyte based on NaBOB dissolved in TMP disclosed promising results in terms of electrolyte ionic conductivity (5 mS cm\(^{-1}\) at room temperature) and electrochemical performance in sodium-ion full cells. Contrary to previous publications where high concentrations of salt or highly fluorinated solvents/additives were used to achieve high Coulombic efficiency on hard carbon anodes, here we have shown that 0.5 M NaBOB in TMP enables relatively high Coulombic efficiency in hard carbon-based full cell sodium-ion cells. The proposed electrolyte can of course be further optimized using electrolyte additives to achieve higher initial Coulombic efficiencies and improved cycle life. As one example, VC has here been shown to improve the electrochemical performance of full-cell sodium batteries using studied electrolyte compositions. Overall, this means that high energy-density cells (>250 Wh kg\(^{-1}\) based on active materials) built from low-cost and abundant materials can be cycled at Coulombic efficiencies above 99%. This in cells with electrolytes that cannot burn using a solvent that freezes at a low -46 °C, without the environmental and health aspects of using highly fluorinated compounds. In short, this work is a promising step to remove most of the problems that of state-of-the-art electrolytes suffer from.

Acknowledgments:

We would like to thank Dr. Andy Naylor for proof reading and scientific discussion. Authors would like to acknowledge the financial support by the ÅForsk Foundation via the grant no. 19-705 and by STandUP for Energy.

Experimental

Materials:

Trimethyl phosphate (99 %) was purchased from Merck and was produced by Acros. Trimethyl phosphate was dried over freshly activated molecular sieves before use in electrolytes. NaBOB was synthesized using the method stated by Zavalij et al.\(^{19}\) with the added step of recrystallizing the synthesized NaBOB in TMP before vacuum drying at 100 °C for more than 12 hours to make sure that the salt was sufficiently dry for use in an electrolyte. The resulting salt was characterized by X-ray diffraction and elemental analysis. Vinylene carbonate was obtained from Gotion Inc. and used as received. Hard carbon anode powder was obtained from a commercial source and used as received while Altris AB supplied the Prussian white (Na\(_x\)Fe[Fe(CN)\(_6\)]) (x>1.8) cathode powder.

Analytical methods:

Elemental analysis was performed by Medac LTD, two equivalent samples were analyzed twice each using CHN combustion analysis & ICP-OES (see supplemental for full report). Conductivity was performed using a Mettler Toledo SevenGo Duo pro pH/ORP/Ion/Conductivity meter SG78 with an InLab 738ISM probe under argon in a glovebox (O\(_2\), H\(_2\)O 1 ppm). Thermogravimetric analysis was performed on a TA Instruments TGA Q500.
under nitrogen flow between room temperature and 600 °C with 5 °C min⁻¹ heat rate. Powder X-ray diffraction measurements were performed in transmission mode on a Stoe & Cie GmbH Stadi X-ray powder diffractometer equipped with a Ge monochromator (single-wavelength Cu Kα1). A Mythen 1 K Si strip detector was operated in sweeping mode with an angular resolution of 2θ = 0.015°. Full details of the rietveld refinement are available in the supplemental information.

Electrolyte preparation:

NaBOB-TMP mixtures with the concentrations 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 mol L⁻¹ were prepared in volumetric flasks. The solutions of 0.3, 0.4, 0.5 M and above required heating (~60 °C) to dissolve while 0.6 M solution remained turbid even after heating. The preparation and heating were performed under argon in a glovebox using a heater/stirrer hotplate.

Flammability test:

The flammability tests were performed on electrolytes by soaking a strip of glass fiber in the electrolyte and exposing it to a butane gas flame in a fume hood. The tests were recorded by mobile phone camera and pictures and times was collected from recordings.

Electrode preparation and cell assembly:

For Prussian white cathodes, the active material, super C65 (C·NERGY) carbon additive and NaCMC binder (Sigma-Aldrich) were mixed in an 85:10:5 ratio by weight, respectively, to this approximately 5 ml distilled water per gram of active material was added before mixing for 1h by planetary ball-mill. The slurry was coated by applicator rod with 150 µm gap, onto 20 µm carbon-coated aluminum foil. Hard carbon anodes were also prepared on carbon-coated aluminum foil using a 95:5 ratio by weight of hard carbon and NaCMC binder with approximately 6 ml distilled water per gram of active material before mixing for 1h by planetary ball-mill and coating with 100 µm gap applicator rod. The anodes and cathodes were both punched into 20 mm in diameter discs with a mass loading of approximately 1.9 mg cm⁻² for PW and 1.1 mg cm⁻² for hard carbon electrodes. The electrodes were dried at 140 °C under vacuum overnight. The cells for galvanostatic cycling used 30 mm diameter Dreamweaver gold (polyaramid fiber) separators and 100 µL electrolyte, while the half-cells, three-electrode cells, and cells for cyclic voltammetry used 30 mm diameter Whatman glass-fiber separators and 200 µL electrolyte, all types were assembled in pouch-cells that were sealed at 2 mBar vacuum. All cell assembly and electrode drying was performed in an argon glovebox with O₂ and H₂O < 1 ppm.

Electrochemical methods:

Galvanostatic cycling for two-electrode cells was performed at 30 mA g⁻¹ (corresponding to 60 µA cm⁻²) between 1 to 3.8 V on a Neware BTS4000 galvanostat while three-electrode cell were cycled on a Biologic MPG2 potentiostat between 1 to 4 V.

Cyclic voltammetry was performed on a Biologic MPG2 potentiostat. The measurements were performed in pouch cells with two electrode cells using a metallic sodium (Aldrich 99.9%) counter electrode or three electrode cells with a Prussian white counter electrode and a Prussian white reference electrode desodiated to 3.3 V vs. Na⁺/Na. Both cell types used a
carbon coated aluminum foil working electrodes and scans were performed using 1 mV s⁻¹ scan speed. Scans started at OCV and were performed between 0 and 4.5 V vs. Na⁺/Na⁺.

XPS Characterization

XPS measurements of cycled electrodes were carried out using a Perkin Elmer PHI 5500 system with the excitation photon energy of 1486.6 eV. The samples were prepared in an Ar-filled glovebox, where cycled cells were opened and rinsed with TMP. Thereafter, the washed samples were gently dried under vacuum over night before being mounted on a sample plate and sealed in a transfer-cup, making it possible to transfer the samples into the XPS without air exposure. The hard carbon electrodes were energy calibrated against the carbon black peak set to 284.4 when visible and secondary carbon peaks when substrate peak was obscured.

References:

(1) Vaalma, C.; Buchholz, D.; Weil, M.; Passerini, S. A Cost and Resource Analysis of Sodium-Ion Batteries. *Nat. Rev. Mater.* 2018, 3 (4), 18013.

(2) Huang, Y.; Zheng, Y.; Li, X.; Adams, F.; Luo, W.; Huang, Y.; Hu, L. Electrode Materials of Sodium-Ion Batteries toward Practical Application. *ACS Energy Lett.* 2018, 3 (7), 1604–1612.

(3) Liu, T.; Zhang, Y.; Jiang, Z.; Zeng, X.; Ji, J.; Li, Z.; Gao, X.; Sun, M.; Lin, Z.; Ling, M.; Zheng, J.; Liang, C. Exploring Competitive Features of Stationary Sodium Ion Batteries for Electrochemical Energy Storage. *Energy Environ. Sci.* 2019, 12 (5), 1512–1533.

(4) Hwang, J.-Y.; Myung, S.-T.; Sun, Y.-K. Sodium-Ion Batteries: Present and Future. *Chem. Soc. Rev.* 2017, 46 (12), 3529–3614.

(5) Huang, Y.; Zhao, L.; Li, L.; Xie, M.; Wu, F.; Chen, R. Electrolytes and Electrolyte/Electrode Interfaces in Sodium-Ion Batteries: From Scientific Research to Practical Application. *Adv. Mater.* 2019, 31 (21), 1808393.

(6) Chawla, N.; Bharti, N.; Singh, S. Recent Advances in Non-Flammable Electrolytes for Safer Lithium-Ion Batteries. *Batteries* 2019, 5 (1), 19.

(7) Ponrouch, A.; Monti, D.; Boschin, A.; Steen, B.; Johansson, P.; Palacín, M. R. Non-Aqueous Electrolytes for Sodium-Ion Batteries. *J. Mater. Chem. A* 2015, 3 (1), 22–42.

(8) Younesi, R.; Veith, G. M.; Johansson, P.; Edström, K.; Vegge, T. Lithium Salts for Advanced Lithium Batteries: Li-Metal, Li-O2, and Li-S. *Energy Environ. Sci.* 2015, 8 (7), 1905–1922.

(9) Xu, W.; Angell, C. A. Weakly Coordinating Anions, and the Exceptional Conductivity of Their Nonaqueous Solutions. *Electrochem. Solid-State Lett.* 2001, 4 (1), E1.

(10) Xu, K.; Zhang, S.; Jow, T. R.; Xu, W.; Angell, C. A. LiBOB as Salt for Lithium-Ion Batteries:A Possible Solution for High Temperature Operation. *Electrochem. Solid-State Lett.* 2002, 5 (1), A26.

(11) Xu, K.; Zhang, S. S.; Lee, U.; Allen, J. L.; Jow, T. R. LiBOB: Is It an Alternative Salt for Lithium Ion Chemistry? *J. Power Sources* 2005, 146 (1–2), 79–85.

(12) Yu, B. T.; Qiu, W. H.; Li, F. S.; Cheng, L. Comparison of the Electrochemical
Properties of LiBOB and LiPF6 in Electrolytes for LiMn2O4/Li Cells. J. Power Sources 2007, 166 (2), 499–502.

(13) Xu, K.; Zhang, S.; Poese, B. A.; Jow, T. R. Lithium Bis(Oxalato)Borate Stabilizes Graphite Anode in Propylene Carbonate. Electrochem. Solid-State Lett. 2002, 5 (11), A259.

(14) Feng, J. K.; Ai, X. P.; Cao, Y. L.; Yang, H. X. Possible Use of Non-Flammable Phosphonate Ethers as Pure Electrolyte Solvent for Lithium Batteries. J. Power Sources 2008, 177 (1), 194–198.

(15) Yu, B. T.; Qiu, W. H.; Li, F. S.; Xu, G. X. The Electrochemical Characterization of Lithium Bis(Oxalato)Borate Synthesized by a Novel Method. Electrochem. Solid-State Lett. 2006, 9 (1), A1.

(16) Xu, K.; Zhang, S.; Jow, T. R. LiBOB as Additive in LiPF6-Based Lithium Ion Electrolytes. Electrochem. Solid-State Lett. 2005, 8 (7).

(17) Zhang, S. S.; Xu, K.; Jow, T. R. Enhanced Performance of Li-Ion Cell with LiBF4-PC Based Electrolyte by Addition of Small Amount of LiBOB. J. Power Sources 2006, 156 (2), 629–633.

(18) Zeng, Z.; Murugesan, V.; Han, K. S.; Jiang, X.; Cao, Y.; Xiao, L.; Ai, X.; Yang, H.; Zhang, J.-G.; Sushko, M. L.; Liu, J. Non-Flammable Electrolytes with High Salt-to-Solvent Ratios for Li-Ion and Li-Metal Batteries. Nat. Energy 2018, 3 (8), 674–681.

(19) Zavalij, P. Y.; Yang, S.; Whittingham, M. S. Structures of Potassium, Sodium and Lithium Bis(Oxalato)Borate Salts from Powder Diffraction Data. Acta Crystallogr. Sect. B Struct. Sci. 2003, 59 (6), 753–759.

(20) Chen, J.; Huang, Z.; Wang, C.; Porter, S.; Wang, B.; Lie, W.; Liu, H. K. Sodium-Difluoro(Oxalato)Borate (NaDFOB): A New Electrolyte Salt for Na-Ion Batteries. Chem. Commun. 2015, 51 (48), 9809–9812.

(21) Wang, L.; Han, W.; Ge, C.; Zhang, R.; Bai, Y.; Zhang, X. Functionalized Carboxyl Carbon/NaBOB Composite as Highly Conductive Electrolyte for Sodium Ion Batteries. ChemistrySelect 2018, 3 (32), 9293–9300.

(22) Yao, X. L.; Xie, S.; Chen, C. H.; Wang, Q. S.; Sun, J. H.; Li, Y. L.; Lu, S. X. Comparative Study of Trimethyl Phosphite and Trimethyl Phosphate as Electrolyte Additives in Lithium Ion Batteries. J. Power Sources 2005, 144 (1), 170–175.

(23) Wang, X.; Yasukawa, E.; Kasuya, S. Nonflammable Trimethyl Phosphate Solvent-Containing Electrolytes for Lithium-Ion Batteries: I. Fundamental Properties. J. Electrochem. Soc. 2001, 148 (10), A1058.

(24) Zeng, Z.; Jiang, X.; Li, R.; Yuan, D.; Ai, X.; Yang, H.; Cao, Y. A Safer Sodium-Ion Battery Based on Nonflammable Organic Phosphate Electrolyte. Adv. Sci. 2016, 3 (9), 1600066.

(25) Zhao, X. M.; Yan, Y. W.; Ren, X. X.; Chen, L.; Xu, S. D.; Liu, S. Bin; Wang, X. M.; Zhang, D. Trimethyl Phosphate for Nonflammable Carbonate-Based Electrolytes for Safer Room-Temperature Sodium-Sulfur Batteries. ChemElectroChem 2019, 6 (4), 1229–1234.

(26) Wang, X.; Yamada, C.; Naito, H.; Segami, G.; Kibe, K. High-Concentration Trimethyl Phosphate-Based Nonflammable Electrolytes with Improved Charge-Discharge Performance of a Graphite Anode for Lithium-Ion Cells. J. Electrochem. Soc. 2006,
153 (1), 135–139.

(27) Wang, J.; Yamada, Y.; Sodeyama, K.; Watanabe, E.; Takada, K.; Tateyama, Y.; Yamada, A. Fire-Extinguishing Organic Electrolytes for Safe Batteries. Nat. Energy 2018, 3 (1), 22–29.

(28) Shi, P.; Zheng, H.; Liang, X.; Sun, Y.; Cheng, S.; Chen, C.; Xiang, H. A Highly Concentrated Phosphate-Based Electrolyte for High-Safety Rechargeable Lithium Batteries. Chem. Commun. 2018, 54 (35), 4453–4456.

(29) Xiao, L.; Zeng, Z.; Liu, X.; Fang, Y.; Jiang, X.; Shao, Y.; Zhuang, L.; Ai, X.; Yang, H.; Cao, Y.; Liu, J. Stable Li Metal Anode with “Ion-Solvent-Coordinated” Nonflammable Electrolyte for Safe Li Metal Batteries. ACS Energy Lett. 2019, 4 (2), 483–488.

(30) Ehlert, T. C.; Hsia, M. M. Thermal Decomposition of Alkali Metal Hexafluorophosphates. J. Chem. Eng. Data 1972, 17 (1), 18–21.

(31) Goodenough, J. B.; Kim, Y. Challenges for Rechargeable Li Batteries. Chem. Mater. 2009, 22 (3), 587–603.

(32) Dahbi, M.; Yabuuchi, N.; Fukunishi, M.; Kubota, K.; Chihara, K.; Tokiwa, K.; Yu, X.; Ushiyama, H.; Yamashita, K.; Son, J.-Y.; Cui, Y.-T.; Oji, H.; Komaba, S. Black Phosphorus as a High-Capacity, High-Capability Negative Electrode for Sodium-Ion Batteries: Investigation of the Electrode/Electrolyte Interface. Chem. Mater. 2016, 28 (6), 1625–1635.

(33) Zeng, Z.; Jiang, X.; Li, R.; Yuan, D.; Ai, X.; Yang, H.; Cao, Y. A Safer Sodium-Ion Battery Based on Nonflammable Organic Phosphate Electrolyte. Adv. Sci. 2016, 3 (9), 1600066.

(34) Dugas, R.; Forero-Saboya, J. D.; Ponrouch, A. Methods and Protocols for Reliable Electrochemical Testing in Post-Li Batteries (Na, K, Mg, and Ca). Chem. Mater. 2019, 31 (21), 8613–8628.

(35) Xu, K.; Lee, U.; Zhang, S.; Allen, J. L.; Jow, T. R. Graphite/Electrolyte Interface Formed in LiBOB-Based Electrolytes I. Differentiating the Roles of EC and LiBOB in SEI Formation. Electrochem. Solid-State Lett. 2004, 7 (9).

(36) Mogensen, R.; Maibach, J.; Naylor, A. J.; Younesi, R. Capacity Fading Mechanism of Tin Phosphide Anodes in Sodium-Ion Batteries. Dalt. Trans. 2018, 47 (31), 10752–10758.

(37) Carboni, M.; Manzi, J.; Armstrong, A. R.; Billaud, J.; Bruttì, S.; Younesi, R. Analysis of the Solid Electrolyte Interphase on Hard Carbon Electrodes in Sodium-Ion Batteries. ChemElectroChem 2019, 6 (6), 1745–1753.

(38) Spori, D. M.; Venkataramanan, N. V.; Tosatti, S. G. P.; Durmaz, F.; Spencer, N. D.; Zürcher, S. Influence of Alkyl Chain Length on Phosphate Self-Assembled Monolayers. Langmuir 2007, 23 (15), 8053–8060.

(39) Eshetu, G. G.; Martinez-Ibañez, M.; Sánchez-Diez, E.; Gracia, I.; Li, C.; Rodriguez-Martinez, L. M.; Rojo, T.; Zhang, H.; Armand, M. Electrolyte Additives for Room-Temperature, Sodium-Based, Rechargeable Batteries. Chem. - An Asian J. 2018, 13 (19), 2770–2780.

(40) Komaba, S.; Ishikawa, T.; Yabuuchi, N.; Murata, W.; Ito, A.; Ohsawa, Y. Fluorinated Ethylene Carbonate as Electrolyte Additive for Rechargeable Na Batteries. ACS Appl. Mater. Interfaces 2011, 3 (11), 4165–4168.
(41) Che, H.; Liu, J.; Wang, H.; Wang, X.; Zhang, S. S.; Liao, X.-Z.; Ma, Z.-F. Rubidium and Cesium Ions as Electrolyte Additive for Improving Performance of Hard Carbon Anode in Sodium-Ion Battery. *Electrochem. commun.* **2017**, 83 (August), 20–23.

(42) Brant, W. R.; Mogensen, R.; Colbin, S.; Ojwang, D. O.; Schmid, S.; Häggström, L.; Ericsson, T.; Jaworski, A.; Pell, A. J.; Younesi, R. Selective Control of Composition in Prussian White for Enhanced Material Properties. *Chem. Mater.* **2019**, 31 (18), 7203–7211.
A schematic of SEI formed on hard carbon in full-cell sodium-ion batteries using 0.5 M NaBOB-TMP or 1 M NaPF$_6$-TMP electrolytes.
Supplemental information

Sodium bis(oxalato)borate (NaBOB) in trimethyl phosphate: a fire-extinguishing, fluorine-free, and low-cost electrolyte for full-cell sodium-ion batteries

Ronnie Mogensen¹, Simon Colbin¹, Ashok Sreekumar Menon¹, Erik Björklund¹, Reza Younesi¹

¹ Department of Chemistry-Ångström Laboratory, Uppsala University, Box 538, SE-75121 Uppsala, Sweden

X-ray diffraction and Rietveld refinement:
The structural characterization of the NaBOB sample was carried out through a Rietveld refinement¹ of the X-ray powder diffraction data against the structure model obtained from Zavalij et al². The refinement was done using Topas Academic (V6) software.³,⁴,⁵ The instrumental parameters (zero error and peak profile function) of the STOE diffractometer were determined by Pawley refinement⁶ of the diffraction data from a Si standard. Thompson-Cox-Hastings (TCHZ_Peak_Type) peak shape function along with an axial divergence macro, Simple_Axial_Model (for the peak asymmetry) was used to model the peak shapes. Average diffracting domain size of the NaBOB particles, which can act an indication of the average crystallite size distribution, was calculated from the sample dependent peak broadening that was modelled through an intermediate Gaussian-Lorentzian function (CS_L and CS_G). It is to be noted that the positions of the atoms and their occupancies were not refined. The isotropic temperature factors (beq) for the atoms were fixed to 1. As mentioned in Zavalij et al., the sample exhibits strong preferred orientation due to the shape of the constituent particles. This was modeled to an extent using spherical harmonics of the fourth order (PO_Spherical_Harmonics), similar to the approach adopted by the authors of the reference. Further details regarding the different functions and macros involved in the refinement can be found in the Topas manual. The structure model obtained after the refinement is shown in the table below.
Table S1. Refined unit cell parameters and atomic structure from the Rietveld refinement of NaBOB.

SLMO (Goodness of fit = 6.75)

Space group: Cmcm

Unit cell parameters

| Atom | Wyckoff site | x/a  | y/b  | z/c  | Occupancy |
|------|--------------|------|------|------|------------|
| Na   | 4c           | 0.9318 | 0.75 | 1.0  | 1          |
| B    | 4c           | 0.4273 | 0.75 | 1.0  | 1          |
| C    | 8f           | 0.2220 | 0.6516 | 1.0 | 1          |
| O    | 8f           | 0.1269 | 0.5642 | 1.0 | 1          |
| O    | 8f           | 0.3440 | 0.5993 | 1.0 | 1          |
| C    | 8g           | 0.0949 | 0.6388 | 0.75 | 1          |
| O    | 8g           | 0.1440 | 0.5173 | 0.75 | 1          |
| O    | 8g           | 0.1756 | 0.7345 | 0.75 | 1          |

S1. Galvanostatic cycling of half-cells of Prussian white vs. Na metal for 0.5 M NaBOB in TMP (a) and 1 M NaPF₆ (b). Cycling was performed between 2 and 4 V at currents corresponding to 0.2 C.
**S2. Discharge capacity vs. cycle number for all the replicates using current density of 30 mA g⁻¹.**

**References**

1. H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, 2, 65–71.

2. M. S. Whittingham, 2003, 753–759.

3. A. A. Coelho, *J. Appl. Crystallogr.*, 2003, 36, 86–95.

4. A. A. Coelho, *Bruker AXS, Karlsruhe, Ger.*

5. A. A. Coelho, J. Evans, I. Evans, A. Kern and S. Parsons, *Powder Diffr.*, 2011, 26, S22–S25.

6. G. S. Pawley, *J. Appl. Crystallogr.*, 1981, 14, 357–361.
| File Name               | Size     | Link Options                       |
|------------------------|----------|------------------------------------|
| PC.mp4 (64.95 MiB)     |          | view on ChemRxiv - download file   |
| TMP 0.5M NaBOB.mp4 (88.48 MiB) |          | view on ChemRxiv - download file   |
| TMP 0.4M NaBOB.mp4 (55.96 MiB) |          | view on ChemRxiv - download file   |
| TMP 0.3M NaBOB.mp4 (62.90 MiB) |          | view on ChemRxiv - download file   |
| TMP 0.2M NaBOB.mp4 (59.83 MiB) |          | view on ChemRxiv - download file   |
| TMP 0.1M NaBOB.mp4 (61.47 MiB) |          | view on ChemRxiv - download file   |
| TMP.mp4 (57.49 MiB)    |          | view on ChemRxiv - download file   |