

Revisiting Amides as Cosolvents for Flame Resistant Sodium Bis(oxalato)borate in Triethyl Phosphate Electrolyte

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In selecting electrolytes for Na-ion batteries, simply importing the analogue of common lithium-ion battery electrolytes to sodium-ion batteries does not address safety concerns like toxicity and flammability. Electrolytes based on sodium bis(oxalato)borate (NaBOB) in organophosphates like triethyl phosphate (TEP) largely alleviate these specific safety concerns. However, it may be beneficial to obtain solutions with higher ionic conductivities than NaBOB in TEP, and compare the performance in Na-ion batteries with high mass loading electrodes. Here, we have shown that N,N-dimethyl formamide (DMF),

N,N-dimethyl acetamide (DMAc), and N-methyl pyrrolidone (NMP) cosolvents almost double the ionic conductivity (from ~3.5 mS/cm to ~7 mS/cm) without sacrificing the flame-retarding properties of the base NaBOB in TEP electrolyte. The physical properties of these cosolvent electrolyte mixtures are investigated, along with the electrochemical performance of these electrolytes full-cells based on hard carbon anodes and Prussian white cathodes with near-commercial areal capacity (~2 mAh/cm²).

Introduction

As electrification of technological sectors increases, energy storage is becoming more and more critical. Lithium-ion batteries (LIBs) have been posited as a revolutionary technology for electric vehicles and electricity grid linked storage, and the LIB field has seen tremendous growth.^[1] There are however current and anticipated hurdles that must be overcome for LIBs. One of the principal concerns regards future demand on Li, which is both expected to be limited in quantity compared to projected need and is also geographically concentrated to relatively small regions.^[2-4] Other concerns involve the safety of batteries as conventional LIBs contain both toxic and flammable compounds^[4-6] and the ethics of resource extraction – particularly Co – required to make state-of-the-art components.^[7]

One alternative is to move away from LIBs altogether, for which sodium-ion batteries (SIBs) hold great promise.^{[3][8]} Whilst SIBs lag behind LIBs in volumetric and gravimetric energy density,^[9,10] they present an opportunity to sidestep the hurdles faced by LIBs with regards to safety, sustainability, and ethical

concerns. Prussian blue analogues, for example, are one of a number of SIB cathodes made from abundant materials and thus mitigate concerns around mineral extraction for use in LIB cathodes.^[11] However, electrolyte toxicity and flammability remain a concern if analogous electrolyte is brought from LIBs to SIBs. Also, conventional LIB electrolytes (i.e., NaPF₆ in a combination of cyclic and/or linear carbonates) are not necessarily the best for SIBs to mitigate dissolution of the solid electrolyte interphase (SEI) in SIBs.^[12]

Recently, sodium bis(oxalato)borate (NaBOB) was shown to be a promising electrolyte salt for SIBs, exhibiting long term cyclability in low mass-loading full-cells composed of Prussian white cathodes and hard carbon anodes.^[13-15] Electrolytes based on NaBOB are fluorine-free (assuming of course that the solvent is fluorine-free) and were shown to have a high decomposition temperature of around 300 °C under N₂ (vs. 140 °C for NaPF₆ under vacuum,^[13,16] although significant capacity loss is observed as low as 55 °C for NaPF₆-based electrolytes),^[13] and showed no sign of Al corrosion.^[13,15] In addition to these benefits, it is thought possible that this could be a low cost and low toxicity salt,^[15] although these claims are yet to be proven conclusively. Despite this promise, two major drawbacks hamper more widespread use of NaBOB based electrolytes: (i) poor solubility in most solvents, and (ii) thick, resistive SEI growth (which although seemingly stable, limits rate performance).^[17]

Of the few solvents that have been shown to provide modest solubility of NaBOB, organophosphates (e.g., trimethyl phosphate (TMP)^[13] or triethyl phosphate (TEP)^[15]) are of particular interest for their flame retardancy and potentially modest toxicity (in the case of TEP^[15]). However, despite showing some solubility in organophosphates, NaBOB is still limited in its solubility (<0.4 M for TMP and TEP) leading to electrolyte conductivities of approximately 5 mS/cm.^[13,15] Previously, N-methyl pyrrolidone (NMP) has shown promise as a cosolvent with TMP, improving the solubility and conductivity

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of the NaBOB based electrolyte without sacrificing performance or flame retardancy.^[14] A modest improvement in rate capability was observed for cells cycled with electrolyte containing NMP as a cosolvent in this study, which was speculated to be the result of the higher conductivities of these electrolytes.

Whilst NaBOB in organophosphate electrolytes have proven successful in low mass loading full cells, with the organophosphate as either a lone or cosolvent, there has been some difficulty in transferring results to high mass loading full cells, particularly with regard to rate performance. Prompted by reports that NaBOB is soluble in N,N-dimethyl formamide(DMF),^[18] in this study we re-evaluate amides (NMP, DMF and N,N-dimethyl acetamide (DMAc)) as cosolvents in TEP-NaBOB electrolytes in SIB full cells with near-commercial areal capacity (approx. 2 mAh/cm²). As previous literature employing an electrolyte with NMP and TMP has pointed out,^[14] it is perhaps confusing to lament the safety concerns of LIBs and then explore the use of three carcinogenic, mutagenic or reprotoxic (CMR) listed cosolvents. This contradiction is unavoidably true, but is tolerated here on the basis that DMF, DMAc and NMP are model solvents, and any results from such study can then be used to guide further research into other, non-CMR amide alternatives. A preliminary search for such alternatives is presented at the end of this paper. In addition, we employ TEP as the base solvent over other organophosphates (e.g., TMP) because of TEP's favourable safety profile.

Results and Discussion

Before evaluating any electrochemical performance of the TEP + cosolvent + NaBOB electrolytes in sodium-ion cells, we first present the physical properties of such electrolytes. The maximum solubilities (and conductivities at these electrolyte concentrations) for NaBOB in TEP, DMF, DMAc and NMP and their mixtures are shown in Figure 1. Note that we opt throughout this paper to use molal concentration (*m*) or wt% to describe electrolyte concentration rather than molar concentration. The equivalent molar concentrations at room temperature are given for comparison in Table S1 and Figure S1. We observe that at room temperature, 5.7 wt% NaBOB could easily be dissolved in TEP (or a molal concentration of 0.28 mol/kg), resulting in an ionic conductivity of 3.5 mS/cm. This concentration can be viewed as a practical saturation limit, which will be used to describe a concentration which can be obtain with ease. However, we have previously shown that through a lengthier process (adding NaBOB to TEP until it remains turbid overnight, followed by slow solvent additions until all salt dissolved) we could produce a 0.367 m solution of NaBOB in TEP that exhibited a room temperature ionic conductivity of 4.44 mS/cm.^[15] As such the reader should be aware that in practise slightly higher concentrations, and by virtue of this slightly higher conductivities, are possible by using an excess of NaBOB and filtering off undissolved NaBOB.

In NMP, the practical solubility limit of NaBOB is equal to 10.9 wt% (0.58 m) at room temperature, providing an ionic

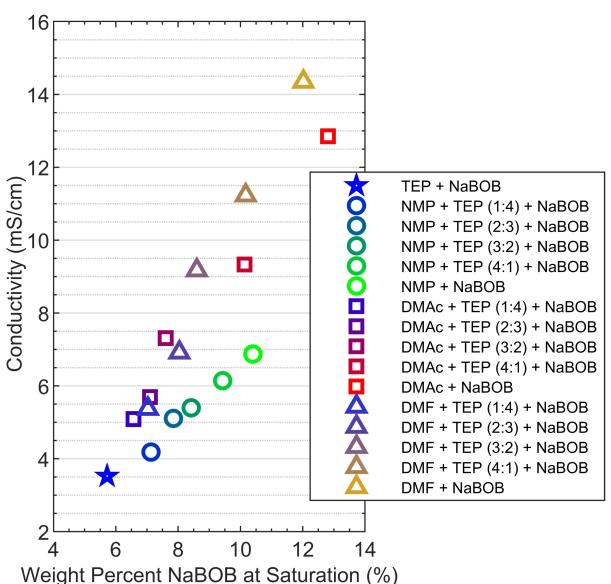


Figure 1. Conductivity at the point of saturation for the NaBOB containing electrolytes. Cosolvent-TEP mixtures refer to v/v ratios of the cosolvent to TEP.

conductivity of 6.9 mS/cm. This is again lower than the 12.8 wt % (0.66 m) solution that we have previously proved is possible, for which the conductivity was observed to be 8.83 mS/cm.^[14] The concentrations of NaBOB in DMF or in DMAc are higher than that in NMP, with maximum practical solubilities of 12.0 wt % (0.65 m) and 12.8 wt% (0.70 m), respectively. These electrolytes show remarkable conductivities of 14.4 mS/cm for DMF + NaBOB and 12.9 mS/cm for DMAc + NaBOB at their respective practical solubility limits at room temperature (~20°C). These ionic conductivities are higher than for LP30 and LP40 electrolyte at 20°C,^[19] and higher than the ionic conductivities for NaPF₆-based electrolytes with equivalent molarities (i.e. 0.65–0.7 m) for all of the solvents (propylene carbonate (PC), NMP, TMP, sulfolane, γ-butyrolactone, γ-valerolactone, monoglyme, tetraglyme, ethyl acetate, methyl acetate, ethyl butyrate, ethyl propionate and methyl propionate) reported by Mogensen et al.^[20] The solubility and corresponding conductivities for the solvent mixtures lie between that of TEP + NaBOB and the corresponding DMF/DMAc/NMP + NaBOB electrolyte, as expected.

The density and viscosity measurements were conducted for the electrolytes in each of the electrolyte cosolvent series, see Figure 2. The DMF and DMAc cosolvent series behaved similarly for both viscosity and density, with the density of saturated TEP + NaBOB (1.09 g/cm³ at 20°C) dropping with greater amounts of DMF or DMAc to 1.00 g/cm³ for both DMF + NaBOB and DMAc + NaBOB at 20°C. Despite what appears as a modest drop in density, it should be noted that for both DMF + NaBOB and DMAc + NaBOB, the solutions contain more than double the wt% NaBOB. Similarly, the viscosity drops from an already modest 2.41 mPas (at 20°C) for TEP + NaBOB to 1.72 mPas for DMAc + NaBOB and 1.35 mPas for DMF + NaBOB. This is of particular significance because NaBOB is insoluble in

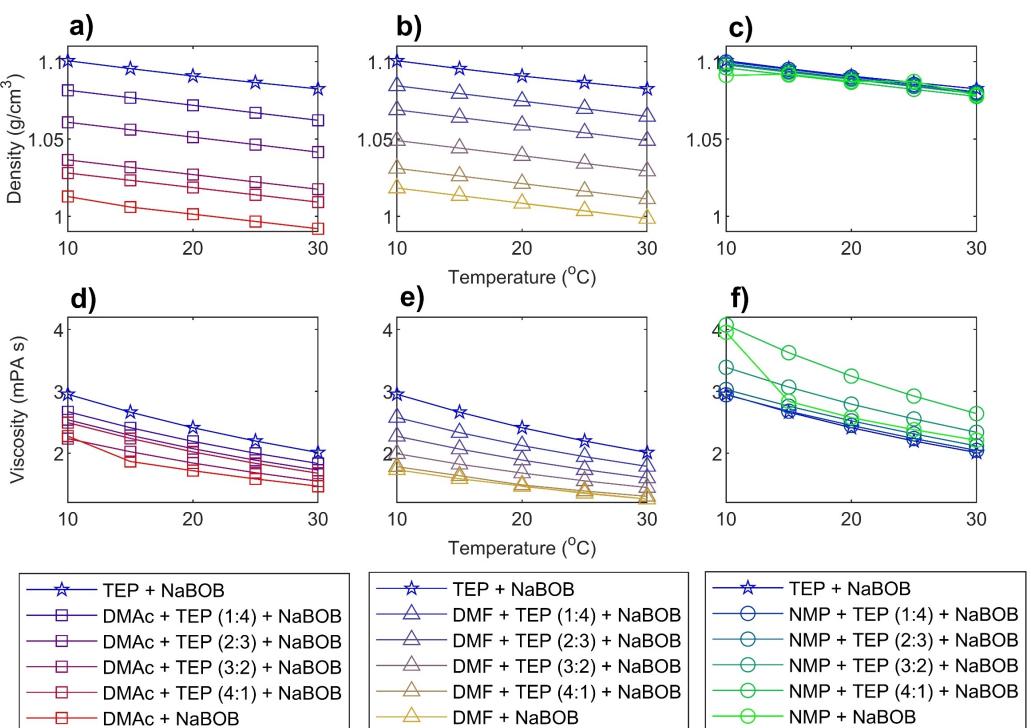


Figure 2. a–c) Density and d–f) viscosity between 10 and 30 °C for electrolytes composed of mixes of a and d) DMAc, b and e) DMF and c and f) NMP with TEP saturated with NaBOB. Cosolvent-TEP mixtures refer to v/v ratios of the cosolvent to TEP.

most solvents used to lower the viscosity of electrolytes. Mixtures containing NMP behaved as expected being both denser and more viscous than DMF or DMAc. Very similar density values were obtained for NMP + NaBOB and TEP + NaBOB, although as noted before it should be kept in mind that NMP + NaBOB had a higher concentration. The viscosity values were likewise similar between the TEP + NaBOB and NMP + NaBOB, but unlike the DMAc or DMF cosolvent series the intermediate mixtures did not smoothly transition in viscosity between both extremes in the series. The viscosity values for all electrolyte compositions compare favourably to commonly used SIB electrolytes. For example, the viscosity of 1 M NaPF_6 in a 1:1 (w/w) mix of ethylene carbonate (EC) and PC at 20 °C was reported to be 6.85 mPas;^[21] for 1 M NaClO_4 in 1:1 (w/w) mix of EC and dimethyl carbonate or dimethoxyethane the viscosity was reported to be slightly above 2 mPas.^[22] Low density, low viscosity electrolytes are beneficial in battery systems comprising high mass-loading electrodes, with the thicker electrodes requiring greater electrolyte amounts to fill all cavities. Firstly, this greater electrolyte volume adversely affects the gravimetric energy density of the cell, and so lower density electrolytes are beneficial to reduce such effects. Secondly, it makes thoroughly wetting the electrodes more difficult, and so lower viscosity electrolytes are typically preferable.

Based on the promising low temperature behaviour shown for both TEP + NaBOB^[15] and NMP + NaBOB^[14] electrolytes, low temperature conductivity measurements were taken for the DMF, DMAc and NMP cosolvent series, shown in Figure 3 (for Arrhenius plots, see Figure S2).^[15] Electrolyte solutions were cooled with liquid N_2 , with conductivity measurements taken as

the electrolytes warmed to room temperature. The DMAc and DMF cosolvent series both showed excellent low temperature conductivity, exhibiting conductivities in the range of 1–5 mS/cm at –20 °C. Of all the electrolyte compositions, the DMF + NaBOB electrolyte shows the most promising low temperature behaviour, maintaining a conductivity of 2.3 mS/cm at –60 °C. By contrast, 1 M NaPF_6 in a 5:3:2 (w/w) mix of EC, PC and DEC was reported to have an ionic conductivity of ~2 mS/cm at –20 °C.^[23]

In order to investigate how much of each cosolvent could be tolerated in the TEP + NaBOB electrolyte before the flame-retardancy was lost, rudimentary flammability tests were conducted with glass fibre separators soaked in electrolyte. Indicative images of the flame tests for the DMAc cosolvent series are shown in Figure 4. The full flammability test videos of all 3 cosolvent series can be found in SI. Three times are compared in Figure 4: the frame before the torch is removed, 5 frames later (equivalent to about 0.17 s assuming that the frame rate is stable at 30 f/s), and 30 frames later (approx. 1 s).

The results of the flame tests for the 3 cosolvent series have been classified into rough categories. Whilst it is common to use self-extinguishing times (SETs) for such flame tests,^[24] such measurement might be misleading for the electrolytes studied here. This is principally because some cosolvent mixtures (e.g., NMP + TEP (4:1, v/v) + NaBOB) could self-extinguish on the first ignition, leading to a low SET, but on second or third ignition burn to completion (or at the least display greater SET). As such, we have categorised the flammability data as follows: (i) 'Very Flammable' – for electrolytes that rapidly burn to completion on the first ignition; (ii) 'Weakly Flammable' – for electrolytes

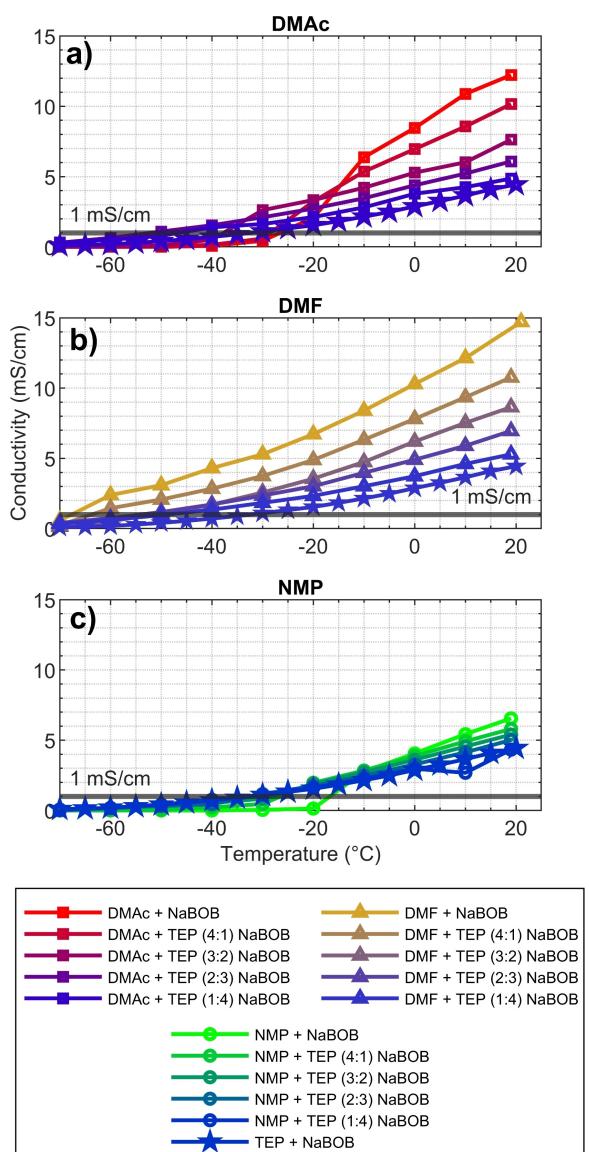


Figure 3. Low temperature conductivity for electrolytes composed of mixes of a) DMAc, b) DMF and c) NMP with TEP saturated with NaBOB. Cosolvent-TEP mixtures refer to v/v ratios of the cosolvent to TEP.

that exhibit self-extinguishing behaviour when first ignited, but on subsequent ignitions instead burn to completion; (iii) ‘Weakly Self-Extinguishing’ – for electrolytes that consistently exhibit self-extinguishing behaviour on first and subsequent ignitions, but which occurs slowly, on the scale of 1 to 3 s; (iv) ‘Self-Extinguishing’ – for electrolytes that consistently exhibit self-extinction rapidly within 1 s, but not immediately after the ignition source is removed; and (v) ‘Flame Retarding & Non-Flammable’ – for electrolytes that self-extinguish immediately when the ignition source is removed (see Figure 5). By these metrics, NMP had to be at or below 60% v/v to be classified as ‘self-extinguishing’, whilst DMF and DMAc had to be kept at or below 40% v/v. It should be noted, flame tests don’t guarantee that a battery will be non-flammable, as shown recently by Jia et al.^[25] We, however, view these experiments as an important

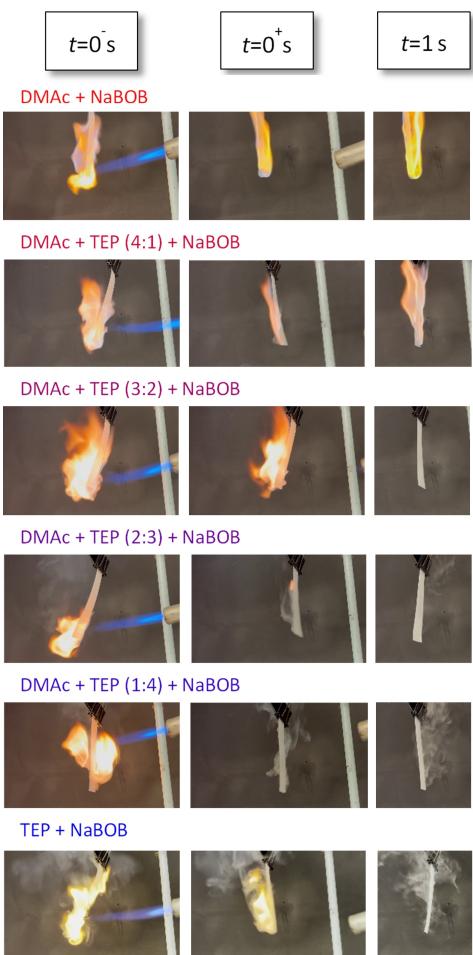


Figure 4. Illustrative flammability test results for the DMAc + TEP electrolyte series (saturated with NaBOB) shown the frame before the flame is removed (left; $t=0^-s$), 5 frames after the flame are removed (middle; $t=0^+s$), equivalent to ~ 0.17 s assuming a constant frame rate of 30 frames per second, and after 1 s (right).

initial step in the suggestion of routes to non-flammable electrolytes.

To test the electrochemical performance of the 3 cosolvent series, each electrolyte composition was tested in full-cells with near-commercial high mass-loading electrodes. The concentrations of each tested solution are shown in Table S1. The cells comprised of a hard carbon anode and a Prussian white cathode (~ 12 mg/cm² cathode mass loading equivalent to ~ 1.8 mAh/cm², with a ~ 7 mg/cm² anode). Figure 6 shows the discharge capacities and corresponding Coulombic efficiencies (CEs) of the first of three formation cycles for each electrolyte composition. For the formation, cells were cycled 3 times with CCCV at C/10 (1 C = 150 mAh/g,^[26] since the cells were cathode limited) with a voltage hold at 3.6 V or 1.3 V until the current subsided below C/100. The median discharge capacity of the first cycle was similar between all cells regardless of electrolyte compositions. For TEP + NaBOB, the median first cycle capacity was 108 mAh/g, lower by ~ 10 mAh/g than that observed for lower mass-loading full cells of hard carbon and Prussian

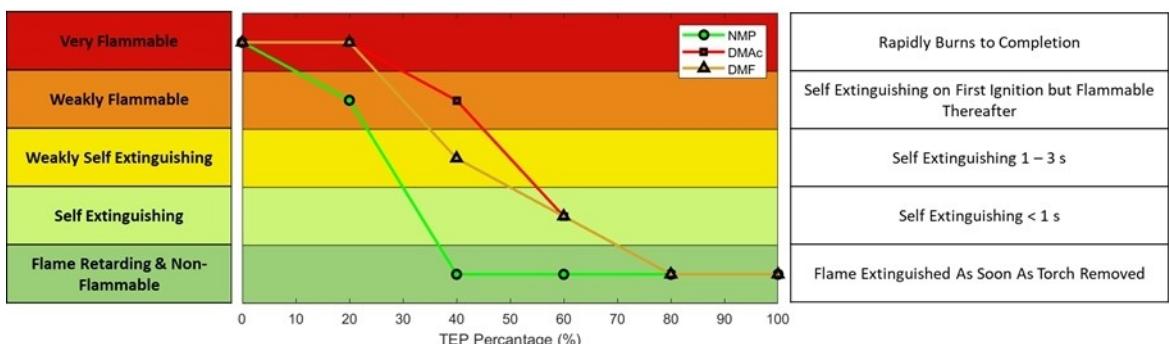


Figure 5. Tolerable cosolvent percentages (v/v with TEP) before the electrolyte mixtures lose their flame-retarding properties. All electrolyte mixtures are saturated with NaBOB. Loosely defined labels (right) are used to group the results of the flame tests.

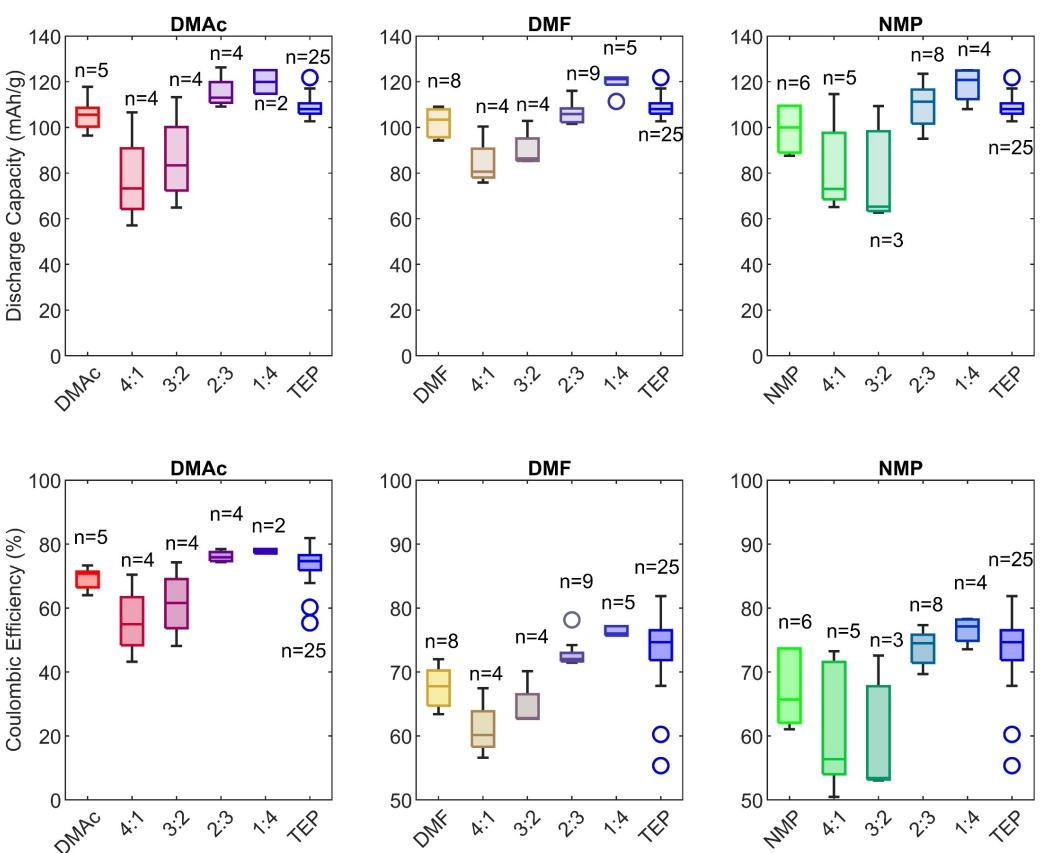


Figure 6. a-c) First cycle discharge capacity and d-f) CE for hard carbon || Prussian white full cells, with a and d) the DMAc + TEP series, b and e) DMF + TEP series and c and f) NMP + TEP series. In all cases, the electrolytes are at the practical solubility limit of NaBOB. Cosolvent-TEP mixtures refer to v/v ratios of the cosolvent to TEP. The number of cells tested, n , is shown for each of the electrolyte compositions. The bars represent non-outlier (set as 1.5 times the interquartile range) maximum and minimum values. The box extents show the upper and lower quartiles, with the line within the box showing the median. Circles indicate data points 1.5 times the interquartile range from the upper or lower quartile.

white.^[15] For the NMP + NaBOB, DMF + NaBOB and DMAc + NaBOB electrolytes, the median first cycle capacities were 100 mAh/g, 103 and 106 mAh/g respectively. Cells with electrolyte compositions with 80% DMAc/DMF/NMP showed the highest median first cycle capacity, which was ~120 mAh/g for all 3 electrolyte compositions. The initial CE was low for all electrolytes, a common feature of NaBOB-based electrolyte.

The capacity-voltage and dQ/dV plots for the first formation cycle of cells made with each of the electrolytes is shown in

Figure 7. The displayed cells were chosen based on those with the median first cycle discharge capacity. Common to all cells is a plateau at a cell voltage of ~1.7 V, which is characteristic of NaBOB decomposition.^[13] The magnitude of the charging in this region roughly followed the electrolyte concentration, in that charging was observed for cells containing the more concentrated electrolytes (See Table S1), i.e., NMP/DMF/DMAc + NaBOB.

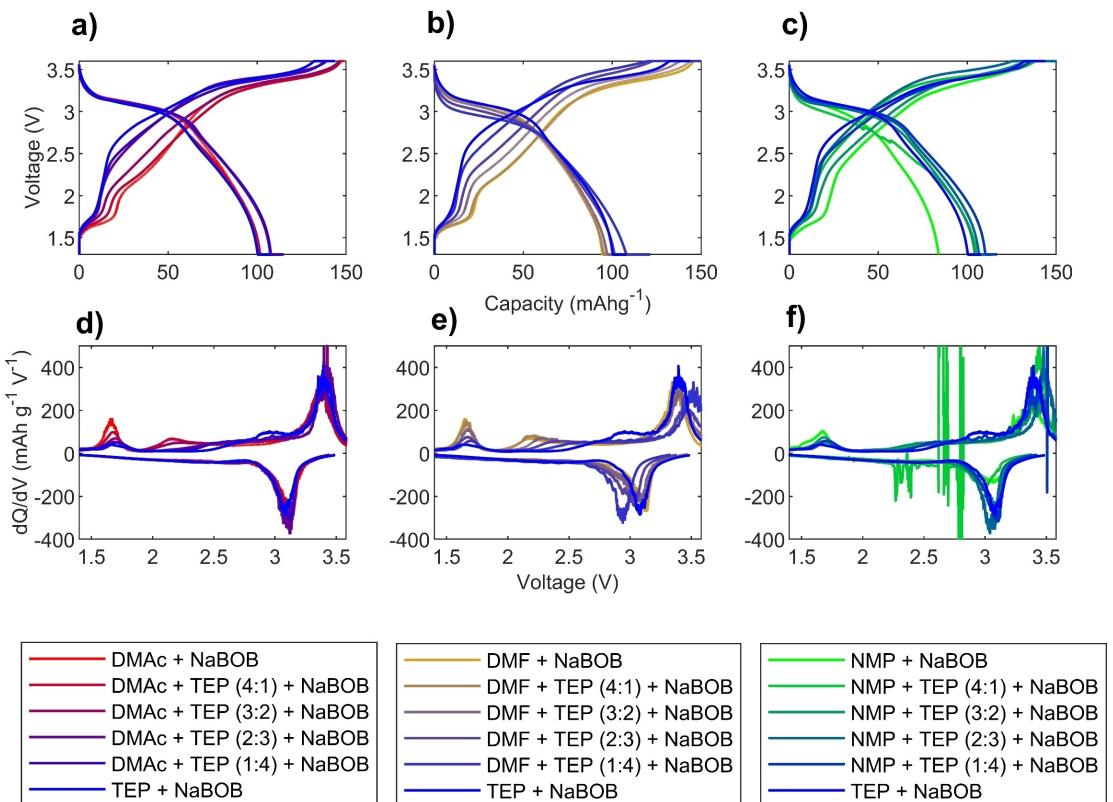


Figure 7. a–c) Capacity–voltage and d–f) dQ/dV plots for the first cycle for electrolytes composed of mixes of a and d) DMAc, b and e) DMF and c and f) NMP with TEP. Cosolvent–TEP mixtures refer to v/v ratios of the cosolvent to TEP, and in all cases electrolytes were saturated with NaBOB.

Capacity fade was observed to be more significant in cells with NMP/DMAc/DMF (either as a lone solvent or as a cosolvent). The capacity over 50 cycles (excluding the 3 formation cycles) at C/10 is shown in Figure 8, comparing cells containing different solvents. Cells with 80% TEP+20% cosolvent (v/v)+NaBOB electrolyte are included as they showed the highest first cycle capacity and retain ‘flame retardancy’ (see Figure 5 and its accompanying discussion). Whilst the 80% TEP+20% cosolvent (v/v)+NaBOB electrolytes exhibited higher capacity during formation, they were outperformed in the longer term cyclability by TEP+NaBOB. Despite rapid capacity fade, the CE remained high in all electrolytes, see Table 1.

The rate capability of cells with TEP+NaBOB is compared with cells that used DMAc+NaBOB, DMF+NaBOB and NMP+

NaBOB in Figure 9. The intermediate cells in each cosolvent series are omitted for clarity. The cell containing the TEP+NaBOB electrolyte showed poor rate capability for C/2 and 1C rates. The rate capability shown here is far poorer than has been shown for Prussian white||hard carbon cells with low mass loading.^[15] In contrast to the cells with TEP+NaBOB electrolyte, cells with DMAc+NaBOB and DMF+NaBOB electrolyte showed greatly improved rate capability. At 1C, the cells with DMAc+NaBOB, DMF+NaBOB and NMP+NaBOB electrolyte retained 43%, 6% and 6% respectively (averaged over the 10 cycles) of the discharge capacity of the first cycle (CCCV at C/10, CV until $I < C/100$). For C/2 cycling, this capacity retention was 64%, 78% and 44% respectively (averaged over the 10 cycles). Despite the auspicious physical properties of the amide-heavy electrolytes (namely greater salt solubility, increased ionic conductivity, lower viscosity and density) electrochemical tests hint towards passivation of the negative electrode impairing cyclability (as noted by Welch et al^[17] for NaBOB containing electrolytes paired with high mass loading electrodes), evidenced here by the low initial coulombic efficiency, poor rate capability and low capacity in comparison to theoretical values.

In an effort to improve the cycling performance, we implement two previously proven strategies to overcome poor rate capability in cells with TEP+NaBOB. Firstly, we use a newly formulated cycling protocol shown to improve the performance of hard carbon||Prussian white cells with TEP+NaBOB

Table 1. Average columbic efficiencies over 50 cycles at C/10, obtained from using each solvent as the sole solvent or as a cosolvent at 20% v/v with TEP.

Solvent	Coulombic efficiency [%]	
	As lone solvent	As cosolvent (20% v/v)
TEP	99.2	-
DMAc	99.1	99.1
DMF	98.8	95.8
NMP	98.6	97.7

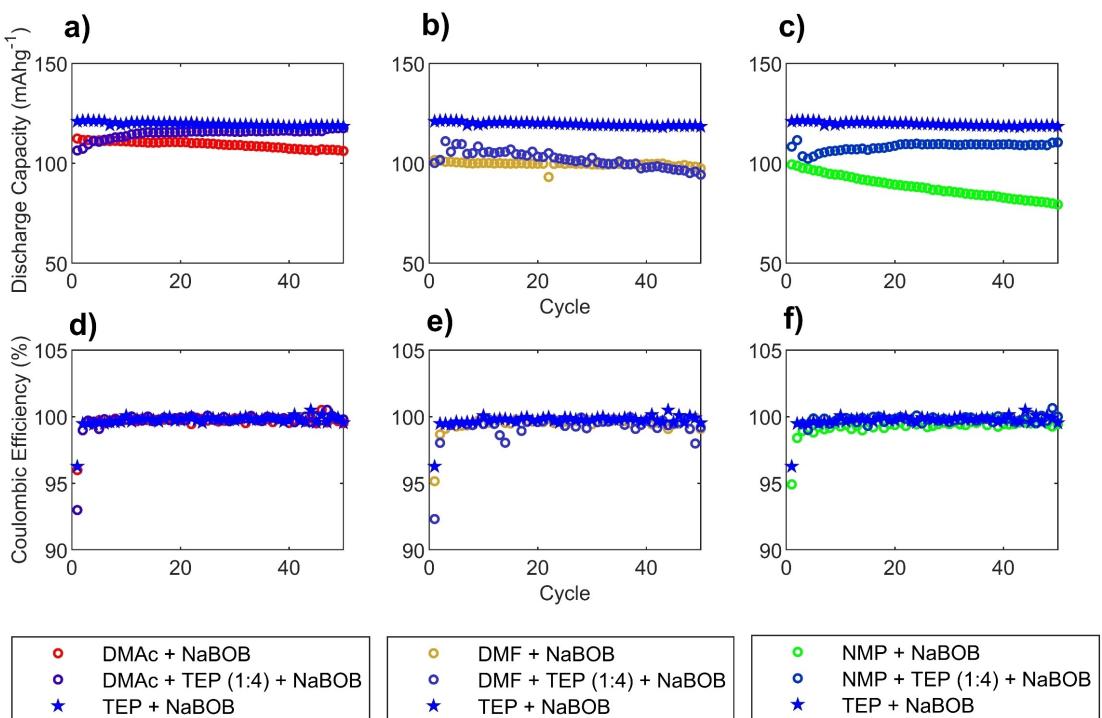


Figure 8. Cyclability plots (C/10) for selected electrolytes in the cosolvent + TEP series (cosolvent-TEP mixtures refer to v:v ratios of the cosolvent to TEP). Comparisons are shown between the cosolvent with NaBOB, TEP with NaBOB, and the cosolvent in a 1:4 ratio (v/v) to TEP. The DMAc series is shown in (a and d), DMF in (b and e) and NMP in (c and f). The three formation cycles are excluded.

electrolyte.^[27] This modified formation protocol is shown in Figure 10, and uses an initial voltage step to 3 V (using 1 C current), followed by standard CCCV formation once the current decays to C/10 during the 3 V hold. That is, during the first charge the cell underwent a CCCV at 1 C with CV at 3 V until $I < C/10$, followed by CCCV at C/10 with CV at 3.6 V until $I < C/100$. Secondly, we use this formation cycling protocol in concert with 5% v/v vinylene carbonate (VC) additive, which has previously been shown beneficial.^[17,20] In order to ensure that the addition of VC doesn't compromise the non-flammability of the TEP + NaBOB electrolyte, flammability testing was conducted in the same fashion as was conducted for the mixed electrolytes. No increase in flammability was observed, with the video included in the SI.

The effect of these interventions on rate capability is shown in Figure 11. The capacity-voltage curves of selected cycles are shown in Figure S3. These interventions are shown here with limited optimisation in order to illustrate the ability to overcome the poor rate capability seemingly inherent to NaBOB-based electrolytes used without any special treatment. The use of the "skip" protocol in concert with 5% v/v VC lead to an improved rate capability, with normalised capacities $> 85\%$ at C/2 for cells with the DMAc + NaBOB, DMF + NaBOB and NMP + NaBOB electrolytes. An improvement in rate capability was also observed for cells with TEP + NaBOB electrolyte using the "skip" protocols and VC additive. It is thus expected that SEI characteristics play a vital role in determining the rate capability in NaBOB-based electrolytes. Still, it is first at C/5 cycling that usable capacities were observed for cells with the TEP + NaBOB

electrolyte using the "skip" protocols and VC additive (at which point the normalised capacity retention was 94%), which hints that rate performance may not be entirely due to SEI characteristics. Whilst this result may hint that the increased ionic conductivity, or perhaps increased salt concentration and by virtue of this increased limiting current, can improve the rate capability of NaBOB-based electrolytes, we have insufficient evidence to make any conclusive guesses. In sum, these results show that without special attention, high rates of cycling cannot be achieved for TEP + NaBOB electrolyte with the Prussian white || hard carbon cells shown here. However, they also show that electrolytes based on NaBOB need not be thought of as inherently incapable of cycling at higher rates.

Finally, we return to the point that DMF, DMAc and NMP are all CMR listed chemicals, which is at odds with the motivation of using lower toxicity electrolytes. These amides were used on the basis of their ubiquity, and were thought to be a good starting point for directing further research on structural analogues with lower toxicity profiles. With such an aim in mind, Figure 12 shows the practical solubility limits and resultant conductivity of NaBOB in 6 alternative amides: N-methoxy-N-methyl acetamide, N,N-dimethyl acetoacetamide, N,N-dimethyl isobutyramide, N,N-dimethyl propionamide, 3-methoxy-N,N-dimethyl propionamide and N-butyl pyrrolidone. The solubility of NaBOB in TEP, DMF, DMAc and NMP is also compared in this figure, shown with bold-faced icons.

These alternative amide solvents were selected on the basis that they show similar enough physical properties to DMF, DMAc and NMP – viz. viscosity, boiling and melting point – but

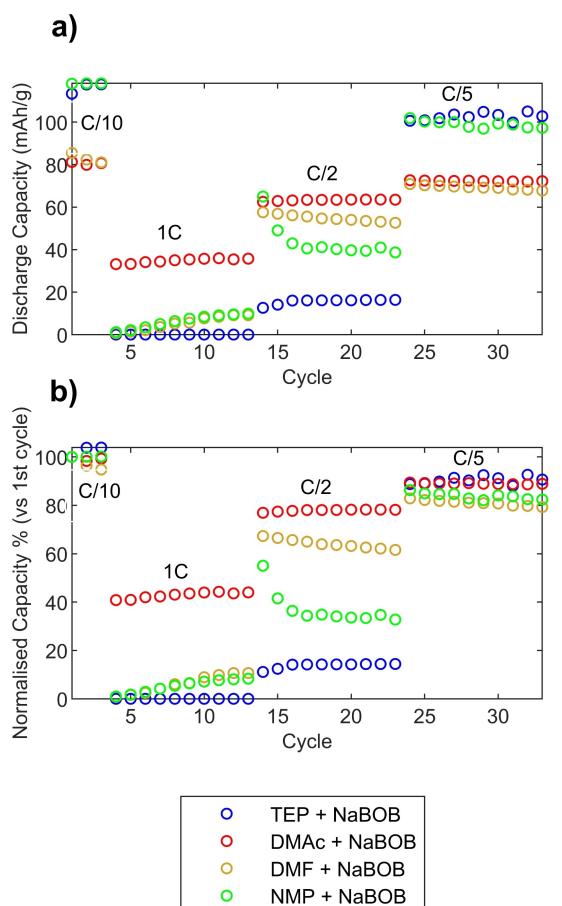


Figure 9. Rate capability of cells containing the TEP + NaBOB, DMAc + NaBOB, DMF + NaBOB and NMP + NaBOB electrolytes. a) The discharge capacities are shown along with b) normalised capacities. For the normalised capacities, the discharge capacity was divided by the first cycle discharge capacity. The first 3 cycles are performed with CCCV charge and discharge (CC at C/10 with CV at 3.6 or 1.3 V until $I < C/100$), whereas the following cycles are all performed using CC.

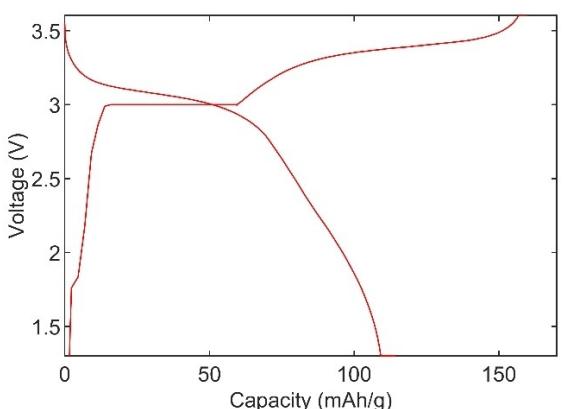


Figure 10. Voltage "skip" formation protocol proposed by Buckel et al.^[27] implemented to attempt to reduce the thick, resistive SEI.

were less of a health hazard. Here it should be noted that a lack of documented toxicity and CMR listing could well be attributed to limited use of these solvents. N,N-dimethyl isobutyramide, N,N-dimethyl propionamide and 3-methoxy-N,N-dimethyl pro-

pionamide are for example listed by the European Chemicals Agency as "substances predicted as likely to meet criteria for category 1 A or 1B carcinogenicity, mutagenicity, or reproductive toxicity, or with dispersive or diffuse use(s) where predicted likely to meet any classification criterion for health or environmental hazards, or where there is a nanoform soluble in biological and environmental media". Hence, whilst these solvents are thought to be more benign than DMF, DMAc and NMP, of those tested only the N-butyl pyrrolidone has been proven to be lower risk.^[28]

Given that only modest cosolvent ratios were seen to be tolerated before flame-retardancy was diminished, it is thought that significantly higher NaBOB solubility and electrolyte conductivity in comparison to TEP is required to make these solvents useful as a cosolvent to TEP. Of the alternative amides, only N,N-dimethyl propionamide showed promise as a cosolvent given its conductivity improvement on the order provided by NMP.

Conclusions

Sodium-ion battery electrolyte composed of NaBOB in TEP is a promising alternative to common carbonate-based electrolytes imported as analogues of LIB electrolytes (i.e., NaPF_6 in carbonates), in that it is non-flammable, relatively low toxicity and fluorine-free. Promising results in sodium-ion cells with low-mass loading electrodes have been difficult to translate to cells with high-mass loading, acting as a barrier to more widespread use. In this study, we have aimed to address these drawbacks by using amide cosolvents for TEP + NaBOB. We investigate DMF, DMAc and NMP as solvents or cosolvents for NaBOB-TEP electrolyte. All the cosolvents improved the solubility of NaBOB, with obtained concentrations of NaBOB in NMP at 0.58 M, at 0.65 M in DMF and at 0.70 M in DMAc. The ionic conductivities were consequently increased to 14.4 mS/cm for DMF + NaBOB, 12.9 mS/cm for DMAc + NaBOB, and 6.9 mS/cm for NMP + NaBOB. These room temperature ionic conductivities for DMF + NaBOB and DMAc + NaBOB are higher than ionic conductivities for LP30 and LP40 electrolytes, despite having nearly half of the salt concentration.

Despite DMAc, DMF and to a lesser extent NMP improving the solubility of NaBOB when used as cosolvents, only modest cosolvent concentrations were permissible to maintain the flame-retardancy that TEP + NaBOB showed. For NMP, cosolvent ratios of up to 60% v/v were acceptable before self-extinguishing behaviour (as we have defined it) was significantly impacted. For DMAc and DMF, this has to be restricted to at most 40% v/v. As a result, despite promising increases in solubility and conductivity from DMF, DMAc and NMP, when considering electrolyte compositions that we consider self-extinguishing only modest increases in solubility and ionic conductivity were achieved.

The electrochemical cycling results of the electrolytes tested in full cells showed similar first cycle capacities (C/10) between all electrolyte solutions. Faster capacity decay was observed in cells with DMAc/DMF/NMP as either a cosolvent or lone solvent.

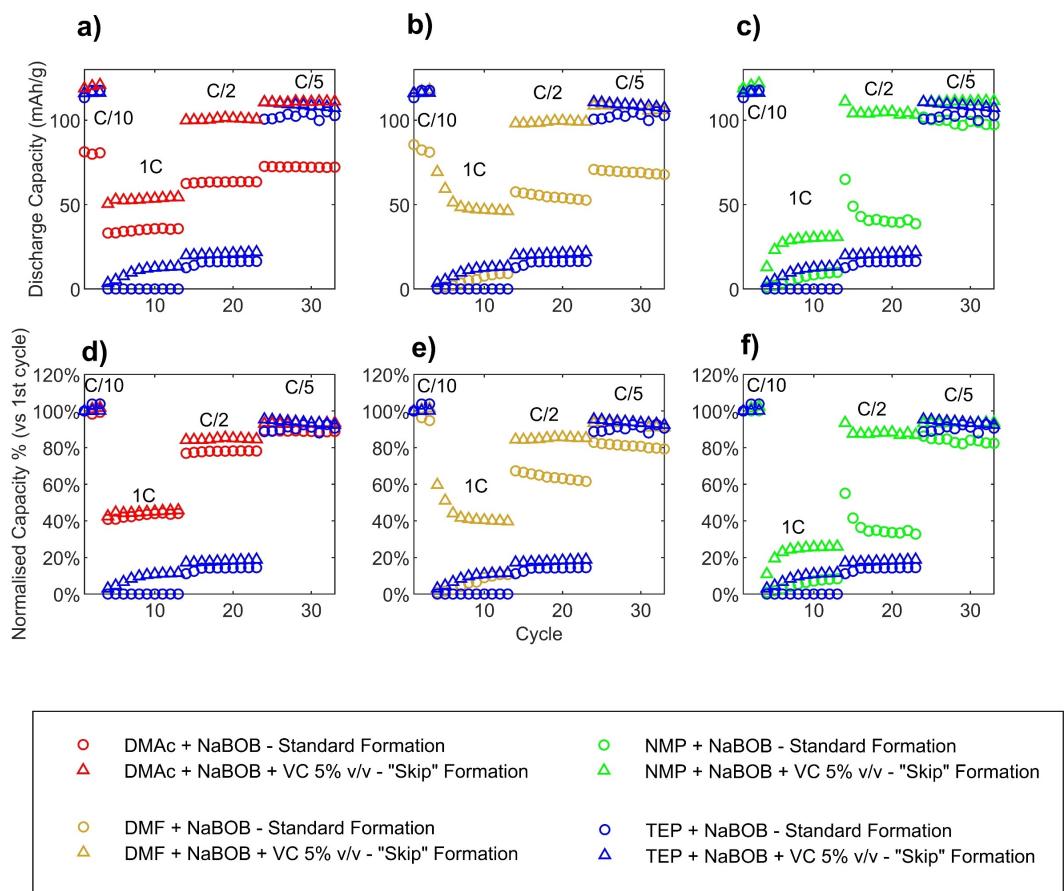


Figure 11. Comparison of a-c) rate capability and d-f) normalised capacity vs. the first cycle discharge capacity for cells with different approaches to combatting poor rate capability due to suspected resistive SEI. Cells formed using the voltage "skip" protocol^[27] with a and d) DMAc, b and e) DMF and c and f) NMP based electrolyte are compared with TEP based electrolyte. These electrolytes are also tested with 5% v/v VC, which is used in combination with the "skip" protocol.

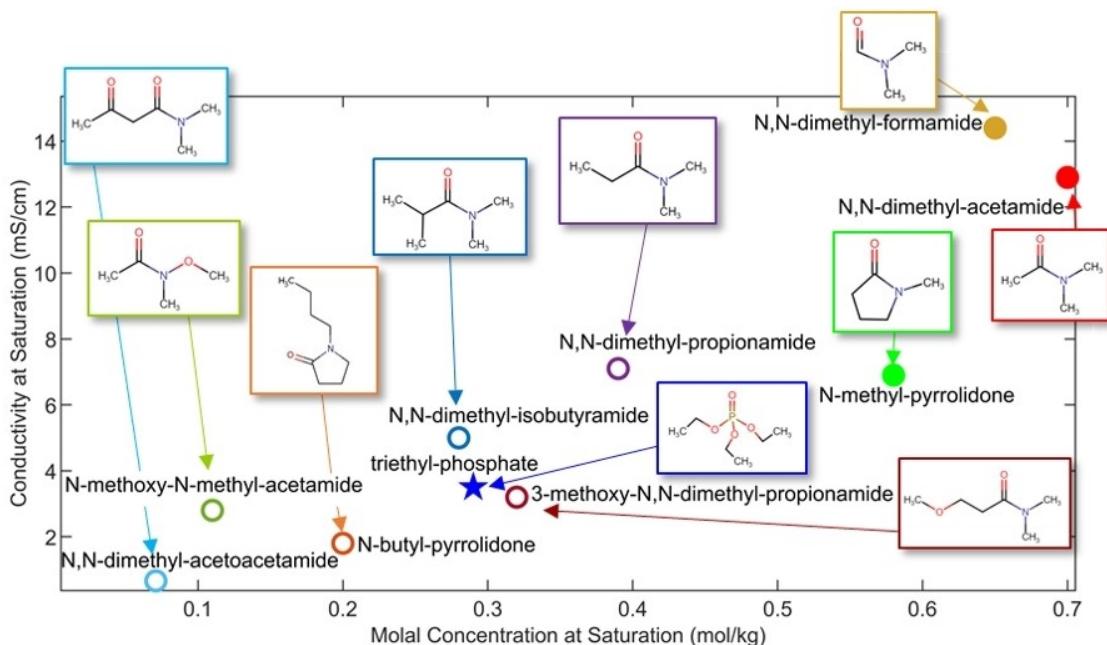


Figure 12. Comparison of the saturation concentration of NaBOB in a range of alternative amide solvents. For each solvent the conductivity is shown at the point of saturation, with a comparison to TEP, DMF, DMAc and NMP saturated with NaBOB.

There was however vast improvement in rate capability for DMF+NaBOB and DMAc+NaBOB in comparison to TEP+NaBOB, with cycling at C/2 capable for DMF+NaBOB and DMAc+NaBOB. By using the "skip" formation protocol proposed by Buckel et al. and using 5% v/v VC as an additive, promising capacities of 51 mAh/g and 53 mAh/g were obtained at 1 C for DMF+NaBOB and DMAc+NaBOB (capacity retentions of 45% and 44% vs. the first cycle discharge capacity at C/10). We have thus demonstrated through this improved rate capability that the sluggish performance of cells with NaBOB-based electrolytes is addressable.

Finally, we have investigated a range of structural analogues of NMP, DMF and DMAc in the search for alternative amide cosolvents with a lower toxicity profile than NMP/DMF/DMAc. Of the alternatives investigated, none of the amides proven to be less toxic showed the promising solubility and ionic conductivity that NMP, DMAc and DMF exhibit. The implication of this is that electrolyte solutions based on NaBOB are more sensitive to the solvent than we anticipated, and one cannot simply take a structural analogue to promising solvents and assume it will perform similarly with regard to NaBOB solubility.

Experimental Section

Materials: TEP (> 99.8%) was produced by Arcos purchased from Merck. Anhydrous DMF (> 99.8%, max. 0.005% H₂O) was produced by VWR Chemicals, anhydrous DMAc (> 99.75%, max. 0.005% H₂O) and anhydrous NMP (> 99.5%, max. 0.005% H₂O) were produced by Thermo Scientific and VC (> 98%, stabilised) was produced by TCI Europe; all four were purchased from VWR. NaBOB was synthesised via the method described by Zavalij et al.^[29] and was further purified as described by Mogensen et al.^[14]

Solubility, conductivity and density measurements: To determine the practical solubility limits of NaBOB in the solvents and solvent mixtures, approx. 5 mL of solvent/solvent mixture were added to a vial and weighed. Solvent mixtures throughout (4:1, 3:2, 2:3 and 1:4) describe v/v mixtures for the cosolvent:TEP. NaBOB was added under stirring until it no longer dissolved. Then the solvent or solvent mixture was slowly added until the NaBOB was fully dissolved. Viscosity and density were determined with an Anton Paar DMA 4100 M with a Lovis 2000ME module at 5 °C increments from 10 °C to 30 °C. Conductivity was measured at room temperature (~20 °C) using a Mettler Toledo SevenCompact Duo with an InLab731 ISM conductivity probe. For low temperature conductivity measurements, the vial containing the electrolyte was placed in a bath of liquid nitrogen with the conductivity probe and temperature probe inserted. Conductivity was measured every 10 °C as the solution heated to room temperature.

Flammability measurements: Strips of Whatman 1820–915 glass fibre separator 2 cm by 11 cm were soaked in 700 µL of electrolyte and suspended lengthwise in a fume cupboard. A Cocraft MRC-982 butane torch was used to ignite the electrolyte. If the sample self-extinguished, the flame was brought back to the separator to reignite it. This procedure was repeated until it was obvious that there was no longer any electrolyte left on the separator. Videos were recorded with a mobile phone camera.

Cell Preparation: Pouch cells were assembled in an Ar filled glovebox (O₂ and H₂O < 0.5 ppm). Electrode sheets of hard carbon and Prussian white coated onto Al were provided by Altris AB. Pouch cell current collectors were made from Al. The electrodes

were punched mechanically outside of the glovebox (20 mm diameter cathodes and 21 mm diameter anodes) and were then subsequently dried under vacuum in the glove box at 170 °C for 15 h. Squares of approx. 3 cm by 3 cm Dreamweaver Gold separator were used. Prior to use, the separators were dried under vacuum in the glovebox at 150 °C over the weekend. Electrolytes were prepared in the glovebox using solvents dried over molecular sieves. Prior to mixing, the solvents were filtered with VWR 0.22 µm pore size Nylon syringe filters dried at 60 °C for 8 h under vacuum in the glove box. Each pouch cell received 120 µL of electrolyte solution, and was then vacuum sealed.

Formation and cycling: Unless otherwise specified, formation was performed with 3 cycles using CCCV at C/10, with a voltage hold at 3.6 V during charge or 1.3 V during discharge until $I < C/100$. After formation, all cycling was performed with CC. Cells were cycled with Neware cyclers at ambient temperature (~20 °C). Pressure was applied with two plastic plates on the front and rear of the pouch cell, held on with bulldog clips.

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Conflict of Interests

The authors declare the following competing financial interest(s): The Prussian white and hard carbon electrodes used in this study were provided by ALTRIS AB, a company founded by R.Y. that A.B. is employed in. The other authors in this paper declare to have no competing interests.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: non-flammable electrolyte • NaBOB • sodium-ion battery • cosolvent

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