Supporting Information

to
A sodium bis(perfluoropinacol) borate-based electrolyte for stable, high-performance room temperature sodium-sulfur batteries based on sulfurized poly(acrylonitrile)

Table S1. Combustion elemental analysis of Na-PPB.

| Element | Calculated (%) | Found (%) |
|---------|----------------|-----------|
| C       | 24.38          | 24.21     |
| H       | 1.279          | 1.318     |
| C : H   | 19.062         | 18.361    |

Table S2. Combustion elemental analysis of an SPAN cathode.

| Element | wt.% | Atomic ratio |
|---------|------|--------------|
|         | S    | C  | N   | H   | C/S |
| SPAN    | 40.24| 42.36| 13.43| 0.9883| 2.81 |
Table S3. Comparison of oxidation potentials of the various existing electrolyte system for RT Na-S batteries.

| Salt / molar | Solvent | Working electrode | Oxidation potential V (vs. Na⁺/Na) |
|--------------|---------|------------------|----------------------------------|
| NaTFSI / 2M  | PC:FEC (1:1) + 10 mM InI₃ | SS | 5.2 [1] |
| NaTFSI / 2M  | TMP:FEC (7:3) | SS | 4.6 [2] |
| NaB(hfip)₄ / 1M | EC:DMC + FEC (1:1) + 13 wt.% | Pt | 4.65 [3] |
| NaCF₃SO₃ / 1M | Triglyme | Carbon-coated Al | 4.0 [4] |
| Na-PPB / 1M  | PC + (FEC, 10 wt.%) | Al | >5.5 (This work) |

Figure S1. Comparison of HOMO and LUMO energy levels of sodium bis(pinacol) borate, NaClO₄, NaTFSI, and Na-PPB.

The calculation of the HOMO and LUMO energy levels was performed with the Gaussian 09 software package using DFT. All energies are calculated at the B3LYP/6-31+G(2d,p) level. We compared the HOMO energy levels of different salts to validate the high oxidation resistance of
Na-PPB. Thus, commercially available salts such as NaClO$_4$ and NaTFSI and a non-fluorinated sodium bis(pinacol) borate HOMO energy levels were calculated and compared with Na-PPB. From Figure S1, it is evident that Na-PPB has a lower HOMO energy level (-8.54 eV) than its counterparts. It is reasonable to associate oxidative stability of the molecule to their HOMO energy level since oxidation results in loosing of an electron from its HOMO. The electron-withdrawing group in the molecule is responsible for lowering the HOMO energy level which in turn increases stability against oxidation. Based on the calculation results, Na-PPB has excellent oxidation stability compared to commercially available sodium salts.

Figure S2. Na||Na symmetrical cell voltage profile at 1 mA cm$^{-2}$ (0.5 mAh cm$^{-2}$) for Na-PPB and Na-hfip.
Figure S3. Cycling performance of a Na-PPB electrolyte with graphite as a working electrode, a) coulombic efficiency (inset: chronopotentiogram); b) comparison of voltage versus capacity plot at various cycles.

Figure S4. $^{19}$F-NMR spectra of a) Na-PPB and b) Na-hfip kept under ambient conditions for 20 days.

Figure S5. Energy profile along the reaction path (NEB calculations) of both salts, representing the potential barrier between two local minima of the respective salt.
Table S4. Comparison of the morphological changes of Na-hfip and Na-PPB after exposure to air for 20 days.

| Samples                        | Na-hfip | Na-PPB |
|--------------------------------|---------|--------|
| Pristine                       | ![Pristine Na-hfip](image1) | ![Pristine Na-PPB](image2) |
| After exposure to air for 20 days | ![After exposure Na-hfip](image3) | ![After exposure Na-PPB](image4) |
| Remarks                        | Color changed to pure white and loss of material | Almost similar to the initial state except for a slight color change |

Table S5. Comparison of the weight loss of Na-PPB and Na-hfip after exposure to air for 20 days.

| Sample  | Initial weight (g) | Weight (g) after 20 days in air | Weight loss (%) |
|---------|--------------------|---------------------------------|-----------------|
| Na-PPB  | 0.0686             | 0.0491                          | 28              |
| Na-hfip | 0.1347             | 0.0128                          | 91              |
| Cathode system        | Electrolyte                                      | C - rate / current | Capacity (mAh g⁻¹) | Cycle life | Coulombic efficiency (%) |
|-----------------------|-------------------------------------------------|--------------------|---------------------|------------|-------------------------|
| Electrospun SPAN      | 0.8 M NaClO₄ in EC + DEC (v = 1:1)              | 1 C                | 153                 | 500        | 99.93 [⁵]               |
| SPAN cathode          | 1 M NaClO₄ in EC + DMC (v = 1:1) + 8 wt% FEC    | 0.5 C              | 1000                | 1000       | ~100 [⁶]                |
| Selenium-doped SPAN   | 1 M NaClO₄ in PC + PC (v = 1:1)                 | 0.4 A g⁻¹          | ~770                | 500        | ~100 [⁷]                |
| Tellurium-doped SPAN  | 1 M NaClO₄ in PC + DMC (v = 1:1) + 10 wt% FEC   | 0.5 A g⁻¹          | ~970                | 600        | ~100 [⁸]                |
| Iodine-doped SPAN     | 1 M NaClO₄ in EC + DEC (v = 1:1) + 8 wt% FEC    | 2 C                | 674                 | 500        | >99 [⁹]                 |
| S / C composite       | 1.5 M NaClO₄ + 0.3 M NaNO₃ in tetraglyme         | -                  | 400                 | 20         | - [¹⁰]                  |
| Sulfur in slit micropore | 1 M NaClO₄ in EC + PC (v = 1:1) + 2 wt% FEC | 1 C                | ~640                | 2000       | ~100 [¹¹]               |
| SPAN cathode          | 1 M Na-PPB in PC + 10 wt%FEC                    | 2 C                | >950                | 500        | >99.8 (This work)       |
References

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