**Sodium-difluoro(oxalato)borate (NaDFOB): A new electrolyte salt for Na-ion batteries**

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**Experiment section**

**Synthesis of NaDFOB**

NaDFOB was synthesized by reacting sodium oxalate (Na$_2$C$_2$O$_4$, Sigma-Aldrich, 99.5%) with boron trifluoride-diethyl-etherate (BF$_3$-ether, ≥46% BF$_3$ basis) in acetonitrile (CH$_3$CN, Sigma-Aldrich, anhydrous, 99.8%). After filtration, the desired product was isolated by removing CH$_3$CN. Further purification was carried out by washing using tetrahydrofuran (THF, Sigma-Aldrich, anhydrous, ≥99.9%). Dry NaDFOB was obtained after removing THF under vacuum. The authors can be contacted for this compound for further development purpose.

**Crystal structure determination**

The powder X-ray diffraction (XRD) pattern of NaC$_2$O$_4$BF$_2$ was collected in capillary mode (Bruker D8 Advance, Cu Kα1, Ge monochromator, 0.01° step, 3s dwell, 6–80 2θ) and indexed in Topas Pro (Bruker AXS; Karlsruhe, Germany). Tetragonal cells such as I4$_1$md, I4$_2$d, P4$_2$mc, and I222 were identified as structure solution candidates. Groups were eliminated if they lacked adequate site symmetry to model the structural moiety or gave a poor fit, P4$_2$mc (weighted profile factor, r$_{wp}$ = 40%) in this case. Molecular subunits were manipulated by density functional theory (DFT) calculations using CASTEP (Accerlys, Inc; San Diego, California, USA). This software package employs a norm-conserving non-local pseudopotential generated by the Kerker scheme, with an energy cut-off of 420 eV. Set parameters: energy charge per atom convergence criterion of 0.00002 eV, root-mean-square displacement of 0.001 Å, and root-mean-square residual force on movable atoms of 0.05 eV/Å. Electron exchange interactions and correlations were modeled following the method developed by Wu and Cohen via a generalized gradient approximation.$^{51}$ The structure was geometry optimized using the Broyden-Fletcher-Goldfarb-Shanno scheme$^{52-54}$, generating atomic coordinates and subsequently, bond geometries. From these, rigid bodies of [C$_2$O$_4$BF$_2$]$^-$ were constructed in Topas and fitted to the X-ray diffraction (XRD) pattern by
Electrolyte and electrode preparation

All tested electrolytes consist of a 1.0 M solution of the salt (NaClO₄, NaPF₆, or NaDFOB) in propylene carbonate (PC hereafter, Aldrich, anhydrous, 99.7%); 5 vol% fluoroethylene carbonate (FEC, Aldrich, 99 %) added PC (PC + 5 % FEC); binary solvent mixtures (50:50 vol%) of ethylene carbonate (EC, Aldrich, anhydrous, 99.0 %) : PC; EC : dimethyl carbonate (DMC, Aldrich, anhydrous, 99.0 %); and EC : diethyl ether (DEC, Aldrich, anhydrous, 99.0 %).

Electrodes for the electrochemical studies were fabricated by mixing the active materials Na₄.₄₄MnO₂, Super P carbon black, and polyvinylidenedifluoride (PVDF) in the weight ratio of 80:10:10. N-Methyl-2-pyrrolidone (NMP) was used as the solvent. The mixture was blended well, and then the slurry was coated uniformly on aluminum foil. After heating at 100 °C for 10 h, the coated foil was cut into disks and assembled into CR2032 coin-type cells with different electrolytes (1.0 M NaDFOB, NaClO₄, or NaPF₆ in PC, PC + 5 % FEC, PC:EC, EC:DEC, or EC:DMC) and a sodium metal disk as counter electrode. The coin cells were assembled in an argon-filled glove box (MBraun, Germany).

Characterization

Elemental analysis of F and B of the as-prepared NaDFOB was carried out on a Dionex Ion Chromatograph ICS-1100 RFIC and inductively coupled plasma (ICP) analyzer, respectively. Fourier transform infrared spectroscopy (FTIR) was conducted on a Shimadzu AIM8000 FT-IR spectrometer. ¹¹B nuclear magnetic resonance (NMR) was performed on a Bruker Avance 400 MHz spectrometer externally referenced to BF₃ at 0.0 ppm. ¹⁹F NMR was performed on a VNMRS PS54 500 MHz spectrometer externally referenced to KF at −125.3 ppm.

Melting points of the electrolytes were determined from differential scanning calorimetry (DSC; TA Q100) curves when the samples were heated from −70 °C to 80 °C at the rate of 10 °C min⁻¹.

The viscosities of the electrolytes were measured with a parallel-plate rheometer (MCR 301, Anton Paar) at 25 °C. The ionic conductivity of the electrolytes was measured with an Oakton CON 11 standard conductivity meter.

Electrochemical performances

The electrochemical stability window of the electrolytes was evaluated using a sodium metal cube slice as the counter and reference electrode and stainless steel as the working electrode. Cyclic
voltammograms (CVs) of cells with electrolytes composed of 1.0 M NaX (X = DFOB, ClO₄, and PF₆) in PC, EC:DEC, and EC:DMC were collected at room temperature at the scan rate of 1 mV s⁻¹.

Galvanostatic charge-discharge tests were conducted on a Neware battery testing system between 4.0 and 2.0 V (versus Na⁺/Na) at room temperature. The Na₀.₄₄MnO₂/Na half-cells using different electrolytes were charged and discharged with a current of 15, 50, 100, 150, 200, 250, 300, and 15 mA g⁻¹ for 6, 21, 21, 21, 21, 21, and 11 cycles, respectively.

Electrochemical impedance spectroscopy (EIS) of the Na₀.₄₄MnO₂/Na half-cells after 143 cycles was conducted on a Biologic VMP-3 electrochemical work station in the frequency range from 10 mHz to 100 kHz at open circuit potential.

![FTIR spectra](image1)

**Fig. S1** FTIR spectra of the as-synthesized NaDFOB compared with commercial Na₅C₂O₄.

![B NMR spectra](image2)

**Fig. S2** ¹¹B NMR spectra of the fresh NaDFOB dissolved in CH₃CN and the solution after storage at room temperature for 120 days. Trace amounts of NaBF₄ was observed in the solution.
Fig. S3 Rietveld refinement of XRD data for NaDFOB. Red is the calculated, black is the observed, and blue is the difference pattern. The short vertical lines: purple is indexed NaBF₄, green is indexed NaDFOB.

Table S1: Lattice and fit parameters for NaDFOB.

<table>
<thead>
<tr>
<th>Compound</th>
<th>NaDFOB</th>
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<tbody>
<tr>
<td>Space group</td>
<td>I₄₁md</td>
</tr>
<tr>
<td>FW (g/mol)</td>
<td>159.8</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>a</td>
<td>7.7316(1)</td>
</tr>
<tr>
<td>b</td>
<td>8.5343(1)</td>
</tr>
<tr>
<td>α, β, γ (°)</td>
<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>510.16(1)</td>
</tr>
<tr>
<td>Rwp (%)</td>
<td>8.21</td>
</tr>
<tr>
<td>Rp(%)</td>
<td>6.53</td>
</tr>
</tbody>
</table>

Table S2: Atomic parameters for NaDFOB. * = Ueq value.

<table>
<thead>
<tr>
<th>Atomic position(s)</th>
<th>Ion</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occ</th>
<th>Uiso (Å²)</th>
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<tbody>
<tr>
<td>Na</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0.3003(7)</td>
<td>1</td>
<td>0.57(8)</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0.6902</td>
<td>1</td>
<td>0.68*</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>8b</td>
<td>0</td>
<td>0.8509</td>
<td>0.5996</td>
<td>1</td>
<td>0.44*</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>8b</td>
<td>0.8908</td>
<td>0</td>
<td>0.9376</td>
<td>1</td>
<td>0.30*</td>
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<tr>
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<td>0.8409</td>
<td>0</td>
<td>0.8007</td>
<td>1</td>
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<td>O2</td>
<td>8b</td>
<td>0.7942</td>
<td>0</td>
<td>0.0638</td>
<td>1</td>
<td>0.20*</td>
<td></td>
</tr>
</tbody>
</table>
Fig. S4 (a) Na\(^+\) cation and (b) DFOB\(^-\) anion coordination environments. \(d_1 = 2.802(4)\) Å, \(d_2 = 2.745(4)\) Å, \(d_3 = 2.570(1)\) Å, \(d_4 = 2.277(5)\) Å. Sodium, oxygen, carbon, boron, and fluorine atoms are represented as green, yellow, black, red, and blue spheres, respectively.

Fig. S5 Crystal structure of NaDFOB. Sodium, oxygen, carbon, boron, and fluorine atoms are represented as green, yellow, black, red, and blue spheres, respectively.
Fig. S6 DSC curves of NaDFOB, NaClO₄, and NaPF₆ in EC:DEC, EC:DMC, EC:PC, PC, and PC + 5% FEC, respectively.

Fig. S7 CV curves of 1.0 M NaX (X =ClO₄ and PF₆) in PC, EC:DMC, and EC:DEC at room temperature at the scan rate of 1 mV·s⁻¹.
Fig. S8 Coulombic efficiencies of Na/Na$_{0.44}$MnO$_2$ half cells containing NaX (X = DFOB, ClO$_4$, PF$_6$)-based electrolytes.

Fig. S9 Viscosity values of 1.0 M NaX (X = ClO$_4$, PF$_6$, and DFOB) in EC:DMC, EC:DEC, EC:PC, PC, and PC + 5% FEC.
Fig. S10 Conductivity of electrolytes consisting of (a) 1.0 M NaClO₄, NaPF₆, and NaDFOB in PC, and (b) 1.0 M NaDFOB in EC:DMC, EC:DEC, EC:PC, PC, and PC + 5 % FEC.

Fig. S11 EIS spectra of Na/Na₀.₄₄MnO₂ half cells in electrolytes composed of 1.0 M NaClO₄, NaPF₆, and NaDFOB in (a) EC:DEC and (b) PC at open circuit potential, which were collected after 143 cycles at different rates.

Fig. S12 ¹¹B NMR spectra of NaDFOB after adding deionized water and aging for 2 min, 2 days, and 6 days.
Fig. S13 $^{19}$F NMR spectra of NaDFOB dissolved in CD$_3$CN, D$_2$O, and the D$_2$O solution stored at room temperature for 2 days.

References