Supporting Information

New class of non-corrosive, highly efficient electrolytes for rechargeable magnesium batteries

Zhirong Zhao-Karger,*a Maria Elisa Gil Bardaji,b Olaf Fuhrb,c and Maximilian Fichtnera,b

aHelmholtz Institute Ulm (HIU), Albert-Einstein-Allee 11, D-89081 Ulm, Germany

E-mail: zhirong.zhao-karger@kit.edu

bInstitute of Nanotechnology, Karlsruhe Institute of Technology (KIT), P.O. Box 3640, D-76021 Karlsruhe, Germany.

cKarlsruhe Nano Micro Facility (KNMF), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany

Experimental

The chemical operations were either carried out on the bench under Ar (99.9999 %) using standard Schlenk techniques (with vacuum of 0.1 Pa) or in a glove box with gas recirculation system, under a controlled argon atmosphere (H₂O and O₂< 1 ppm). All the dried chemicals including anhydrous solvents were stored in glovebox. MgBr₂ (Sigma-Aldrich) was dried at 120 °C under vacuum for 24 h. The fluorinated alcohols were purchased from abcr GmbH or Sigma-Aldrich and dried over 4 Å molecular sieves. NaBH₄ and Ca(BH₄)₂∙2THF were purchased from Sigma Aldrich and used as received. NaAlH₄ (Alfa Aesar) was purified prior
to use. The glyme solvents were purchased from Sigma-Aldrich and dried over 3 Å or 4 Å molecular sieves.

Powder X-ray diffraction (XRD) patterns were recorded in the 2θ range 10-75° using a Philips X’pert diffractometer equipped with Cu Kα source. Scanning electron microscopy (SEM) was performed with a LEO 1530 at 15 keV using carbon tape as the substrate. \(^{1}\)H, \(^{13}\)C and \(^{27}\)Al NMR spectra were recorded with a Bruker Advance II 500 spectrometer. The \(^{13}\)C NMR spectra were broadband \(^{1}\)H decoupled. A 1 M solution of Al(NO)\(_3\) in D\(_2\)O was used as the reference for the \(^{27}\)Al NMR. THF-\(d_8\) or CDCl\(_3\) were used as solvents for NMR measurements and the chemical shifts were reported in ppm using the residual solvent peak as the reference.\(^3\) X-ray single crystal diffraction was performed with a Stoe StadiVari diffractometer using Cu-Kα (\(\lambda = 1.54186\) Å) radiation. Using Olex2\(^1\), the structure was solved with the ShelXS\(^2\) structure solution program using Direct Methods and refined with the ShelXL\(^3\) refinement package using Least Squares minimization.

**Synthesis of Mg[B(hfip)\(_4\)]\(_2\) by reaction 1**

Finely ground Mg(BH\(_4\))\(_2\) powder (0.54 g, 10 mmol) was dissolved into 25 mL DME in a two necked Schlenk flask. The flask was equipped with a Dimroth condenser because the reaction is exothermic and hexafluoroisopropanol [HOC(H)(CF\(_3\))\(_2\)] has a low boiling point (59 °C). 8.5 equivalents of HOC(H)(CF\(_3\))\(_2\) (14.4 g, 9 mL, 85 mmol) were dropwise added over a period of 1 h into the stirred solution of Mg(BH\(_4\))\(_2\). The reaction mixture was stirred at r.t. for 20 h. Then the solvent was removed by vacuum and the solid was dried in vacuum at 40 °C for 1 d yielding 14.6 g (88 %) of the product.

\(^{1}\)H-NMR (500.28 MHz, \(d_8\)-THF): \(\delta = 3.27\) (s, DME-CH\(_3\)), 3.43 (s, DME-CH\(_2\)), 4.72 (m, CH).

\(^{19}\)F NMR (470.73 MHz, \(d_8\)-THF, H-decoupled): \(\delta = -75.4\) (CF\(_3\)). \(^{11}\)B NMR (160.51 MHz, \(d_8\)-THF, H-decoupled): \(\delta = 1.66\). MS-ESI [B(OC(H)(CF\(_3\))\(_2\)]\(_4\)] \(678.95\), Cal. C\(_{12}\)H\(_4\)BF\(_2\)O\(_4\) \(678.98\).
Crystallographic data for Mg[B(hfip)$_4$]$_2$·3DME: Mr = 1652.59; space group C2/c; $a = 22.044(1)$ Å; $b = 66.069(3)$ Å; $c = 22.156(1)$ Å; $\alpha = 90^\circ$; $\beta = 106.575(4)^\circ$; $\gamma = 90^\circ$; $V = 30928(3)$ Å$^3$; $Z = 20$; $T = 130$ K; colourless rod; crystal size: 0.23 x 0.70 x 0.23 mm; $\rho_{\text{calc}} = 1.775$ g cm$^{-3}$; $\mu$(Cu-K$\alpha$) = 2.141 mm$^{-1}$; 36942 reflections measured ($2\Theta_{\text{max}} = 110^\circ$), 18274 ind. refl. ($R_{\text{int}} = 0.0387$, $R_\sigma = 0.0507$), 13195 refl. with $I > 2\sigma(I)$; $GoF = 1.111$, $R_1(I > 2\sigma(I)) = 0.1032$, $wR_2$(all data) = 0.2278; CCDC no. 1537493.

Table S1. List of the fluorinated alkyloxyborate based Mg compounds.

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Formula</th>
<th>Mg borates</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1,1,3,3,3-Hexafluoro-2-propanol</td>
<td>(CF$_3$)$_2$CHOH</td>
<td>Mg[B(OCH(CF$_3$)$_2$)$_2$]$_2$</td>
<td>MgBOR(hfip)</td>
</tr>
<tr>
<td>1,1,1,3,3,3-Hexafluoro-2-methyl-2-propanol</td>
<td>CH$_3$C(CF$_3$)$_2$OH</td>
<td>Mg[B(OC(CH$_3$)(CF$_3$)$_2$)$_2$]$_2$</td>
<td>MgBOR(hfmip)</td>
</tr>
<tr>
<td>1,1,1,3,3,3-Hexafluoro-2-phenyl-2-propanol</td>
<td>C$_6$H$_5$C(CF$_3$)$_2$OH</td>
<td>Mg[B(OC(C$_6$H$_5$)(CF$_3$)$_2$)$_2$]$_2$</td>
<td>MgBOR(hfphpip)</td>
</tr>
<tr>
<td>Trifluoromethyl-2-propanol</td>
<td>CF$_3$C(CH$_3$)$_2$OH</td>
<td>Mg[B(OC(CH$_3$)$_2$(CF$_3$)$_2$]$_2$</td>
<td>MgBOR(tfmip)</td>
</tr>
<tr>
<td>Perfluoro-tert-butyl alcohol</td>
<td>(CF$_3$)$_3$COH</td>
<td>Mg[B(OC(CF$_3$)$_3$]$_2$</td>
<td>MgBOR(pftb)</td>
</tr>
<tr>
<td>Perfluoropinacol</td>
<td>[(CF$_3$)$_2$C(OH)]$_2$</td>
<td>Mg[B(OC(CF$_3$)$_2$C(CF$_3$)$_2$O)]$_2$</td>
<td>MgBOR(pfpina)</td>
</tr>
</tbody>
</table>

Preparation of the electrolyte comprised of Mg[B(hfip)$_4$]$_2$ in diglyme–tetraglyme

Mg(BH$_4$)$_2$ powder (0.216 g, 4 mmol) was dissolved into 5 ml of diglyme–tetraglyme (1:1) in a Schlenk flask equipped with a Dimroth condenser. 8.5 equivalents of HOC(H)(CF$_3$)$_2$ (5.73 g, 3.6 ml, 34 mmol) were dropwise added over a period of 0.5 h into the stirred solution of
Mg(BH$_4$)$_2$. The reaction mixture was stirred at r.t. for 40 h. Then the volatile unreacted HOC(H)(CF$_3$)$_2$ was removed under vacuum with stirring for overnight. The resulting 0.8 M colourless solution was used as electrolyte. The concentration was calculated on the basis of the amount of Mg(BH$_4$)$_2$ used.

**Synthesis of Mg[B(hfip)$_4$]$_2$ by metathesis reaction 2**

*Step 1: Synthesis of Na[B(hfip)$_4$]* According to the literature procedures,$^4$ finely ground NaBH$_4$ powder (1.0 g, 26.43 mmol) was dissolved in 50 mL DME in a two necked Schlenk flask equipped with a Dimroth condenser. 4.3 equivalents of HOC(H)(CF$_3$)$_2$ (19.10 g, 12 ml, 113.7 mmol) were slowly added over a period of 1 h into the stirred solution of NaBH$_4$ in DME. After stirring at r.t. for 0.5 h, the reaction mixture was refluxed for 4 h. The solvent was then removed by vacuum; the product was dried at first at r.t. and then at 43 °C for 20 h in vacuum (0.1 Pa). 20.2 g of Na(DME)[B(hfip)$_4$] was obtained in yield of 95%.

*Step 2: Metathesis reaction* 21.606 g (2.0 mmol) of Na(DME)[B(hfip)$_4$] was dissolved in 2.5 ml of DME. Then 0.184 g (1.0 mmol) of MgBr$_2$ was added. The mixture was stirred for 1 d at r.t. The white precipitates were filtrated. The colourless filtrate was characterized with MS and used as electrolyte.

**Preparation of Mg[Al(hfip)$_4$]$_2$**

*Step 1: Synthesis of Na[Al(hfip)$_4$]* Na[Al(hfip)$_4$] was prepared following related literature procedures with some modifications.$^5$ Commercially available NaAlH$_4$ was purified prior to use. Typically 5 g of NaAlH$_4$ was dissolved in 80 mL THF in a Schlenk flask and stirred at r.t. for overnight. Then the suspension was filtrated. The solid residues were extracted with 40 ml THF again. The clear filtrates were combined and subsequently dried under vacuum yielding about 3.6 g of white NaAlH$_4$ powder.
To a suspension of NaAlH$_4$ (1.43 g, 2.65 mmol) in hexane (60 ml) was dropwise added HOC(H)(CF$_3$)$_2$ (19.15 g, 11.65 mmol, 12 ml) in a period of 1 h. The mixture was slowly heated to reflux and gas evolution was observed during this time. After stirring for another 6 h under reflux, white gel like solids appeared. The solvent and other volatiles were removed under vacuum to yield the white solid 18.3 g (95 %). MS [Al(hfip)$_4$]$^-$ 694.93; Cal. C$_{12}$H$_4$AlF$_{24}$O$_4$ 694.95

Step 2: Metathesis reaction 31.436 g (2 mmol) of Na[Al(hfip)$_4$] was dissolved in 2.5 ml of DME. Then 0.184 g (1 mmol) of MgBr$_2$ was added. The mixture was stirred for 1d at r.t. The white participates were filtrated. The colourless filtrate was characterized with MS and used as electrolyte.

Synthesis of Ca[B(hfip)$_4$]$_2$

Commercial Ca(BH$_4$)$_2$·2THF powder (1.07 g, 5.0mmol) was dissolved into 10 ml DME in a two necked Schlenk flask equipped with is a reflux condenser. 8.5 equivalents of HOC(H)(CF$_3$)$_2$ (7.14 g, 4.5 mL, 42.5 mmol) were dropwise added over a period of 0.5 h into the stirred solution of Ca(BH$_4$)$_2$. The reaction mixture was stirred at r.t. for 20 h. Then the solvent was removed by vacuum and the solid was dried in vacuum at 40 °C for 1 d yielding solid product. MS [B(hfip)$_4$]$^-$ 678.95; Cal. C$_{12}$H$_4$BF$_{24}$O$_4$ 678.98

Electrochemistry Electrochemical studies were performed in Swagelok type cells. The fabrication of all electrodes and the construction of the electrochemical cells were carried in an argon-filled glove box. Cyclic voltammograms were obtained using a Biologic VMP-3 potentiostat with a two-electrode cell comprising a Pt disc as working electrode, Mg foil as reference electrode at a scan rate of 25 mV s$^{-1}$. The conductivity was determined with a Metrohm 917 conductometer at 25 °C.
Cathodes were prepared by coating the slurry (75 % S/CMK-3 composite, 15 % carbon black, 10 % CMC binder) on the stainless steel current collectors and dried at 40 °C for 24 h. 250 -μm-thick Mg foil (99.9%) was used as the negative electrode and a borosilicate glass fiber sheet GF/C as separator. The cells were placed in an incubator to maintain a constant temperature of 25 ± 0.1 °C. The electrochemical studies were carried out using an Arbin battery cycling unit.

Fig. S1 $^{11}$B NMR
**Fig. S2.** Cyclic voltammograms of the 0.8 M MgBOR(hfip)/DME solutions using Pt as working electrode and Mg as reference at a scan rate of 25 mV s\(^{-1}\).

**Fig. S3** Coulombic efficiency of the 0.8 M MgBOR(hfip)/DME solutions. Inset shows the chronopotentiograms.
Fig. S4. Cyclic voltammogram of the 0.45 M MgAlOR(hfip)/DME solutions at the 5th cycle using Pt as working electrode and Mg as reference at a scan rate of 25 mV s⁻¹.

MS spectra
NMR spectra
References