A Stable, Non-Corrosive Perfluorinated Pinacolatoborate Mg Electrolyte for Rechargeable Mg Batteries**

Jian Luo*, Yujing Bi+, Liping Zhang, Xiaoyin Zhang, and Tianbiao Leo Liu*

Dedicated to Prof. Marcella Y. Darenbourg on the occasion of her 77th birthday

Abstract: Mg batteries are a promising energy storage system because of the physicochemical merits of Mg as an anode material. However, the lack of electrochemically and chemically stable Mg electrolytes impedes the development of Mg batteries. In this study, a newly designed chloride-free Mg perfluorinated pinacolatoborate, Mg[B(O$_2$C$_2$(CF$_3$)$_2$)$_2$]$_2$ (abbreviated as Mg-FPB), was synthesized by a convenient method from commercially available reagents and fully characterized. The Mg-FPB electrolyte delivered outstanding electrochemical performance, specifically, 95% Coulombic efficiency and 197 mV overpotential, enabling reversible Mg deposition, and an anodic stability of up to 4.0 V vs. Mg. The Mg-FPB electrolyte was applied to assemble a high voltage, rechargeable Mg/MnO$_2$ battery with a discharge capacity of 150 mAhg$^{-1}$.

Electricity of modern society, including portable devices, electrical vehicles, and grid-scale storage, has driven intensive research into the development of inexpensive, safe, long-cycling life, high performance energy storage technologies. Recently, a great deal of effort has been focused on developing low cost and high energy density, rechargeable batteries beyond lithium (Li) ion batteries using abundant alkaline or alkaline earth metals as anode materials. Magnesium (Mg) batteries are a promising electrochemical energy storage system because of the attractive technological merits of the Mg anode: it is safe (mild reactivity), environmentally benign, inexpensive (approximately 24 times cheaper than Li), it has a high theoretical capacity (2205 Ahkg$^{-1}$ or 3832 AhL$^{-1}$ vs. 3861 Ahkg$^{-1}$ or 2062 AhL$^{-1}$ for Li), and a high reduction potential (−2.37 vs. SHE). However, the research into rechargeable Mg batteries is still in its infancy, and development of Mg batteries is primarily hampered by two grand challenges, the lack of high performance Mg$^{2+}$ electrolyte and energy-dense cathode materials.

As Mg$^{2+}$ electrolytes play a pivotal role in rechargeable Mg batteries, intensive efforts have been made in developing high-performance Mg$^{2+}$ electrolytes in the past decade. The reported Mg$^{2+}$ electrolytes applied in Mg batteries are mainly based on the combination of a Mg-containing Lewis base (for example, Grignard reagents and MgCl$_2$) and a Lewis acid (for example, AlCl$_3$ and AlP$_3$), known as Mg-chloride complex electrolytes as their active species are characteristic of Mg–Cl coordination moieties. The most well-known Mg-chloride complex electrolyte contains [$\mu$-Cl$_2$Mg(THF)$_5$]$^+$ dimer monocation as the active species. However, chloride-containing Mg-chloride complex electrolytes are corrosive and not chemically compatible with high-voltage cathode materials and/or common current collectors (for example, stainless steel, SS, or aluminium, Al). Thus, developing stable and simple Mg$^{2+}$ salts, free of chloride like those used in Li ion batteries, is of great need but remains extremely challenging. A few examples of chloride-free Mg salt electrolytes have been reported for reversible Mg deposition/striping while achieving high anodic stability (up to 4.0 V vs. Mg), including Mg(CB$_3$H$_5$)$_2$,$^3$ Mg(CB$_3$H$_5$)$_2$F,$^4$ Mg[Al(HFIP)$_3$]$^5$ and Mg[B(HFIP)$_3$]$_2$ (HFIP = OCH(CF$_3$)$_2$).$^6$ However, Mg(CB$_3$H$_5$)$_2$ is expensive and not suitable for broad Mg battery applications because the synthesis of carborane anion (CB$_3$H$_5^-$)-containing precursors is not trivial and they are very expensive with very limited commercial availability. Mg[B(HFIP)$_3$]$_2$ lacks chemical stability under ambient conditions as it undergoes chemical decomposition in the presence of moisture, which is believed to be the same for Mg[Al(HFIP)$_3$]$_2$. Therefore, the development of chloride-free Mg electrolytes from inexpensive commercially available chemicals is required to simultaneously deliver excellent electrochemical performance and chemical stability. Herein, we report a highly electrochemically active, anodically stable, and non-corrosive magnesium fluorinated pinacolatoborate, Mg[B(O$_2$C$_2$(CF$_3$)$_2$)$_2$]$_2$ (abbreviated as Mg-FPB, Figure 1), which has strongly coordinating perfluorinated pinacolato bidentate ligands to stabilize the boron center. The Mg-FPB electrolyte delivered outstanding electrochemical performance, specifically, 95% Coulombic efficiency and 197 mV overpotential ($\eta$) for reversible Mg deposition, and anodic stability up to 4.0 V vs. Mg in diglyme (DGM). Furthermore, the Mg-FPB electrolyte was used to produce a 2.0 V high voltage Mg/MnO$_2$ battery.

To develop chloride-free Mg salt electrolytes, a key consideration is the choice of the weakly coordinating anions because they need to be electrochemically and chemically stable to enable a wide voltage window and electro-
chemical/chemical compatibility with electrode materials.[26] Furthermore, Mg salts with a weaker anion–cation interaction give higher solubility and ionic conductivity in their electrolyte solutions.[4a,5] In light of strong B–O bonds (809 kJ mol⁻¹)[3c,8] and the chelating effect of polydentate ligands, we sought to employ chemically stable B anions supported by bidentate alkyloxide ligands in developing chloride-free Mg salt electrolytes. We first attempted the idea by reacting Mg(BH₄)₂ with pinacol (2,3-dimethyl-2,3-butanediol). However, the reaction could not go completion to form magnesium bispinacolatoborate, Mg[B(O₂C₂(CH₃)₄)]₄₂. Because of a high pKₐ (approximately 18) of the alcohol protons of pinacol, NMR spectroscopy studies indicate that pinacol only undergoes partial deprotonation by BH₄⁻, even in refluxed DME (Supporting Information, Figure S1). Furthermore, the resulting solution is not electrochemically active for Mg deposition (Supporting Information, Figure S1).

Then we examined a perfluorinated pinacol (hexafluoro-2,3-ditrifluoromethyl-2,3-butanediol) as a bidentate alkyloxide ligand precursor. Due to the strong electron-withdrawing effect of –CF₃ groups, the perfluorinated pinacol is expected to have more acidic protons to allow complete deprotonation with BH₄⁻. The reaction of 1:4 ratio of Mg(BH₄)₂ and the perfluorinated pinacol readily proceeded to completion at 60°C in DME to yield magnesium fluorinated pinacolatoborate, Mg[B(O₂C₂(CF₃)₄)]₄₂ (abbreviated as Mg-FPB) in a good isolated yield of 93% on a greater than 10 g reaction scale (Figure 1A). Mg-FPB salt was fully characterized by ¹¹B-NMR and ¹⁹F-NMR spectroscopy, and elemental analysis. Mg-FPB displays a single resonance in the ¹⁹F-NMR (70.36 ppm) and ¹¹B-NMR (13.36 ppm) spectra (Figure 1B,C), which is consistent with the expected tetrahedral geometry of the FPB anion. It was found that the Mg-FPB salt has a good solubility of 0.5 M in DGM. The molecular structure of Mg-FPB solvated by DGM was unambiguously determined by single-crystal X-ray diffraction (Figure 1D). In the X-ray diffraction determined structure, the Mg ion is coordinated by two meridional tridentate DGM in an octahedral geometry and paired with two tetrahedral FPB anions for charge neutrality.

A 0.5 M Mg-FPB electrolyte in DGM (3.95 mScm⁻¹ conductivity) was subsequently studied for its electrochemical activity for Mg deposition/stripping. As shown in the cyclic voltammogram (CV, Figure 2A), the Mg-FPB electrolyte displayed a reversible Mg deposition/stripping wave with an onset potential at ~0.308 V vs. Mg and a stripping potential at
Mg-FPB electrolyte was also under the same conditions (Supporting Information, Figure S8) electrolytes Mg-FPB electrolyte displayed nearly 100% Mg
electrolyte has an excellent cathodic stability due to the (V, vs. Mg) electrochemical stability chemical stability

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$\eta$ (mV)</th>
<th>CE (%)</th>
<th>$E_{\text{anod}}$ (V, vs. Mg)</th>
<th>Electrochemical stability</th>
<th>Chemical stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-FPB</td>
<td>197</td>
<td>95</td>
<td>4.0</td>
<td>negligible fluoride deposition</td>
<td>stable with moisture</td>
</tr>
<tr>
<td>Mg[B(HFIP)$_4$]</td>
<td>267</td>
<td>83</td>
<td>4.0</td>
<td>fluoride deposition</td>
<td>decompose with moisture</td>
</tr>
</tbody>
</table>

$-0.111\,\text{V}$, giving overpotential of $197\,\text{mV}$, which is comparable with Mg/MgCl$_2$/AlCl$_3$ (MMAC) electrolytes,[10] but lower than reported chloride-free Mg electrolytes.[4–7] A high Coulombic efficiency of 95% was obtained at $50\,\text{mV/s}$ with a glassy carbon electrode (Supporting Information, Figure S2). Furthermore, the Mg-FPB electrolyte exhibited an outstanding anodic stability at more than $4.0\,\text{V}$ vs. Mg, which is comparable with reported chloride-free Mg electrolytes.[4–7] but significantly improved over other reported Mg electrolytes.[26]

Chloride-containing Mg electrolytes are corrosive to common metallic current collectors, such as SS and Al, which makes them not practically attractive.[24] In stark contrast, the Mg-FPB electrolyte displayed a high anodic stability of approximately $4.0\,\text{V}$ vs. Mg with a variety of working electrodes, including SS, titanium (Ti), and Al (Figure 2B). All of them demonstrated reversible Mg deposition with Coulombic efficiencies of 81% for SS, 83% Ti, and 95% for Al (Supporting Information, Figure S3). Furthermore, when Mg was used as a working electrode, as shown in Figure S3D in the Supporting Information, the Mg plating/stripping was extremely smooth, as no overpotential was observed. The CV of the Mg-FPB electrolyte was also measured in non-ethereal solvents, such as MeCN (Supporting Information, Figure S5); however, no reversible Mg deposition/stripping behavior was observed, which indicates that solvents strongly affect the electrochemical activity of the Mg electrolyte.

Subsequently, a symmetric Mg/0.5 M Mg-FPB/Mg cell was assembled to evaluate the long-term electrochemical performance of the Mg-FPB electrolyte, as shown in Figure 3 A, B. The symmetric cell was tested from $50\,\mu\text{A/cm}^2$ to $1.0\,\text{mA/cm}^2$ current density. At $50\,\mu\text{A/cm}^2$ current density, the polarization was observed at approximately $70\,\text{mV}$. Even when the current density was increased to $1.0\,\text{mA/cm}^2$, the polarization was still below $100\,\text{mV}$ (approximately $90\,\text{mV}$ vs. Mg). The high rate performance of the Mg-FPB electrolyte is attributed to the designed non-coordinating FPB anion that has weak interaction with Mg$^{2+}$ and enables fast electrochemical decomposition and stripping. The symmetric cell was further cycled at $0.1\,\text{mA/cm}^2$ for 500 hours and demonstrated highly stable polarization (Figure 3B). The stable polarization during galvanostatic cycling demonstrates that the Mg-FPB electrolyte has an excellent cathodic stability due to the stable FPB anion.

To investigate the beneficial effects of the chelating FPB ligand in the Mg-FPB over the monodendate ligand used in the reported Mg[B(HFIP)$_4$], electrolyte,[7a] we also conducted CV studies of Mg[B(HFIP)$_4$] under the same conditions (Supporting Information, Figure S2). It was found that Mg-[B(HFIP)$_4$] displayed a larger overpotential (267 mV) and lower Coulombic efficiency (83%) for Mg deposition/stripping than Mg-FPB although they both have comparable cathodic stability (Table 1). The Mg deposition/stripping reversibility of the Mg-FPB electrolyte is much better than that of Mg[B(HFIP)$_4$] (Supporting Information, Figures S2 and S4). Furthermore, in the symmetric cell studies, the Mg[B(HFIP)$_4$] electrolyte manifested much higher overpotential (Supporting Information, Figure S6 and S7), which is consistent with the literature.[14] The Mg[B(HFIP)$_4$] electrolyte took approximately 150 hours to reach comparable overpotential as Mg-FPB. In the bulky electrochemical Mg deposition studies, both Mg-FPB (Figure 3C) and Mg[B(HFIP)$_4$] (Supporting Information, Figure S8) electrolytes yielded a smooth and dendrite free Mg layer. The energy-dispersive X-ray (EDX) spectrum of the Mg layer deposited from the Mg-FPB electrolyte displayed nearly 100% Mg deposition with negligible F (Figure 3C). However, in the EDX spectrum of the deposited Mg layer from Mg[B(HFIP)$_4$], there was 12.5% C, 9.9% O, and 1.9% F, which clearly indicates the electrochemical decomposition of the [B(HFIP)$_4$] anion during the Mg plating process.

![Figure 3](image-url)
Furthermore, the chemical stability of the Mg-FPB and Mg[B(HFIP)₂] electrolytes was further compared by exposure to moisture (1% or 10000 ppm water added). As shown in Figure S9 in the Supporting Information, the Mg-FPB electrolyte remained a clear solution after water treatment for two days, and its ²⁷F-NMR spectrum remained unchanged, which indicates the high chemical stability of the FPB anion against hydrolysis. However, the Mg[B(HFIP)₂] electrolyte changed from a clear solution to a white gel. A new signal at ~76.45 ppm chemical shift was observed in the ²⁷F-NMR spectrum, which clearly indicates the decomposition of the [B(HFIP)₂]⁻ anion. The observed superior electrochemical and chemical stability of Mg-FPB over Mg[B(HFIP)₂] is attributed to the stabilization effect of the perfluorinated pinacolato bidentate ligand. Furthermore, albeit subject to further mechanistic studies, we hypothesize that the acidic proton on the alpha carbon of the HFIP substituent may be also responsible for the inferior performance of the Mg[B(HFIP)₂] electrolyte.

Finally, we conducted preliminary studies of an Mg/MnO₂ battery to further demonstrate the anodic stability of the Mg-FPB electrolyte in Mg ion batteries. Due to the high anodic stability of the Mg-FPB electrolyte (greater than 4.0 V vs. Mg), the Mg/MnO₂ battery was charged up to 3.9 V, as shown in Figure 4 (green curves). The Mg/MnO₂ Mg ion battery delivered a 2.0 V battery voltage and 150 mAh g⁻¹ discharge capacity at a current density of 10 μA g⁻¹. However, the Mg/MnO₂ battery using chloride-containing MMAC electrolyte[9] was constantly charged at 1.1 V due to the lower anodic stability and corrosion of the electrolyte at the Al current collector while delivering a negligible discharge capacity (Figure 4, red curves).

Figure 4. The representative charge/discharge curves of Mg-MnO₂ batteries using 0.5 M Mg-FPB electrolyte in DGM (green) and 0.5 M MMAC (red) at 10 μA g⁻¹ current density.

In conclusion, a new chloride-free Mg electrolyte with non-coordinating perfluorinated pinacolatoborate counter anions was developed and comprehensively studied by NMR spectroscopy, single crystal X-ray diffraction, and electrochemical studies. The Mg-FPB electrolyte exhibited outstanding electrochemical performance for Mg plating/striping with an overpotential of 197 mV, a Coulombic efficiency of 95%, and an anodic stability above 4.0 V with a variety of current collectors. It is believed that the Mg-FPB electrolyte, with its excellent chemical and electrochemical stabilities, will find broad applications in Mg batteries. Furthermore, the molecular design of the Mg-FPB electrolyte with the consideration of highly stable perfluorinated chelating ligands for the counter anion will inspire the development of new electrolytes not limited to Mg²⁺.

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Conflict of interest

A patent including the reported results has been filed.

Keywords: energy storage · magnesium electrolytes · magnesium batteries · perfluorinated pinacolatoborate

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