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

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Abstract

Mg batteries are a promising energy storage system because of physicochemical merits of Mg metal as an anode material. However, the lack of electrochemically and chemically stable magnesium electrolytes impedes the development of Mg batteries. In this study, a newly designed chloride-free magnesium fluorinated pinacolatoborate, $\text{Mg}[\text{B}((\text{CF}_3)_4\text{C}_2\text{O}_2)_2]_2$ (abbreviated as **Mg-FPB**), was synthesized by convenient methods from commercially available reagents and fully characterized. The **Mg-FPB** electrolyte delivered outstanding electrochemical performance, specifically, 95% coulombic efficiency and 197 mV overpotential for reversible Mg deposition, and anodic stability up to 4.0 V vs Mg. The **Mg-FPB** electrolyte was applied to demonstrate a high voltage rechargeable Mg/MnO₂ battery with a discharge capacity of 150 mAh/g.

Graphical Abstract

Keywords

Magnesium electrolytes; perfluorinated pinacolatoborate; Mg battery; energy storage

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Supporting Information. The Supporting Information is available free of charge on the ACS Publications website. Experimental procedures, post-cell NMR and CV analysis, cell impedance spectroscopy, battery data.

Electrification of modern society including portable devices, electrical vehicles, and grid-scale storage has driven intensive research development of inexpensive, safe, long-cycling life, high performance energy storage technologies.¹ Recently, a great deal of effort has been focused on developing low costs and high energy density rechargeable batteries beyond 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 their attractive technological merits: being safe (mild reactivity), environmentally benign, inexpensive (ca. 24 times cheaper than Li), high capacity (2205 Ah/kg or 3832 Ah/L vs 3861 Ah/kg or 2062 Ah/L for Li), and high reduction potential (-2.37 vs SHE).²⁻⁴ However, the research of rechargeable Mg batteries is still in the infancy stage, and their development are primarily hampered by two great challenges, the lacks of high performance Mg^{2+} electrolyte³⁻⁴ and energy-dense cathode materials.²

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.⁵⁻¹³ The reported Mg^{2+} electrolytes applied in Mg batteries are mainly based on the combination of a magnesium containing Lewis base (e.g. Grignard reagents and MgCl_2) and a Lewis acid (e.g. AlCl_3 and AlPh_3), known as Mg-chloride complex electrolytes as their active species are characteristic of Mg-Cl coordination moieties.³⁻⁴ The most well-known Mg-chloride complex electrolytes contains $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ dimer mono-cation as active species.⁴ However, chlorides contained in Mg-chloride complex electrolytes are corrosive and not chemically compatible with high voltage cathode materials and/or common current collectors (e.g. stainless steel or Al).³⁻⁴ 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.⁴ There are a few rare examples of Cl-free Mg salt electrolytes reported for reversible Mg deposition while achieving high anodic stability (up to 4.0 V vs Mg), including $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$,¹⁴⁻¹⁵ $\text{Mg}(\text{CB}_{11}\text{H}_{11}\text{F})_2$,¹⁶ $\text{Mg}[\text{Al}(\text{HFIP})_4]_2$,¹⁷ and $\text{Mg}[\text{B}(\text{HFIP})_4]_2$ ($\text{HFIP} = -\text{OCH}(\text{CF}_3)_2$).¹⁸⁻¹⁹ However, $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ is expensive and not suitable for broad Mg battery applications because the synthesis of carborane anion ($\text{CB}_{11}\text{H}_{12}^-$) containing precursors are not trivial and they are very pricy with very limited commercial availability. And $\text{Mg}[\text{B}(\text{HFIP})_4]_2$ lacks of good chemical stability at ambient conditions as it undergoes chemical decomposition with moisture,¹⁸ which is believed same as $\text{Mg}[\text{Al}(\text{HFIP})_4]_2$. Therefore, it is highly demanding to develop new Cl-free Mg electrolytes from inexpensive commercially available chemicals to deliver high electrochemical performance and excellent chemical stability simultaneously. Herein, we report highly electrochemically active, anodically stable, and non-corrosive magnesium fluorinated pinacolatoborate, $\text{Mg}[\text{B}((\text{CF}_3)_4\text{C}_2\text{O}_2)_2]_2$ (abbreviated as **Mg-FPB**, Figure 1), which is featured with strongly coordinating perfluorinated pinacolatoborate bidendate ligands to stabilize the boron center. The **Mg-FPB** electrolyte delivered outstanding electrochemical performance, specifically, 95% coulombic efficiency and 197 mV overpotential for reversible Mg deposition, and anodic stability up to 4.0 V vs Mg. In addition, the **Mg-FPB** electrolyte was applied to demonstrate a 2.0 V high voltage Mg/MnO₂ battery.

To develop Cl-free Mg salt electrolytes, a key consideration is the choice of the weakly coordinating anions because they need to be electrochemical and chemically stable to enable

wide voltage window and electrochemical/chemical compatibility with electrode materials.³ In addition, Mg salts with weaker anion–cation interaction give higher solubility and ionic conductivity in their electrolyte solutions.^{14, 16} In light of strong B–O bonds (809 kJ/mol)^{7, 20} and the chelating effect of polydentate ligands, we have sought to employ chemically stable B anions supported with bidentate alkyoxide ligands in developing Cl-free Mg salt electrolytes. We first attempted the idea by reacting $\text{Mg}(\text{BH}_4)_2$ with pinacol (hexafluoro-2,3-dimethyl-2,3-butanediol). However, the reaction could not go completion to form magnesium bispinacolato borate, $\text{Mg}[\text{B}((\text{CH}_3)_2\text{C}(\text{O}_2)_2)_2]_2$. Because of a high pK_a (ca. 18) of the alcohol protons of pinacol, NMR studies indicate that pinacol only undergoes partly deprotonation by BH_4^- even in refluxed DME (Figure S1). In addition, the resulting solution is not electrochemically active for Mg deposition (Figure S1).

We then used a perfluorinated pinacol, (hexafluoro-2,3-difluoromethyl-2,3-butanediol), as a bidentate alkyoxide ligand precursor. Due to the strong electron-withdrawing effect of $-\text{CF}_3$ groups, the perfluorinated pinacol is expected to have more acidic protons to proceed complete deprotonation with BH_4^- . The reaction of 1:4 ratio of $\text{Mg}(\text{BH}_4)_2$ and the perfluorinated pinacol readily proceeded to completion at 60 °C in DME to yield magnesium fluorinated pinacolatoborate, $\text{Mg}[\text{B}((\text{CF}_3)_2\text{C}(\text{O}_2)_2)_2]_2$ (abbreviated as **Mg-FPB**) in a good isolated yield of 87% (Figure 1A). **Mg-FPB** salt was fully characterized by ^{11}B -NMR, ^{19}F -NMR, and elemental analysis. **Mg-FPB** displays a single resonance in the ^{19}F -NMR (70.36 ppm) and ^{11}B -NMR (111.36 ppm) spectra (Figure 1B and 1C), 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 diglyme (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 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 mS/cm conductivity) was subsequently studied for its electrochemical activity for Mg deposition/stripping. As shown in the cyclic voltammogram (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 -0.111 V, giving overpotential of 197 mV which is comparable with MMAC electrolytes¹⁰ but smaller than reported Cl-free Mg electrolytes.^{14–19} A high coulombic efficiency of 95% was obtained at 50 mV/s with glassy carbon electrode (Figure S2). Furthermore, the **Mg-FPB** electrolyte exhibited an outstanding anodic stability at > 4.0 V vs Mg, which is comparable with reported Cl-free Mg electrolytes,^{14–19} but significantly improved over other reported Mg electrolytes.⁴

Chloride contained Mg electrolytes are corrosive with common metallic current collectors, such as stainless steel (SS) and aluminum (Al), which makes them not practically attractive.⁴ In a stark contrast, the **Mg-FPB** electrolyte displayed high anodic stability of ca. 4.0 V vs Mg with a variety of working electrodes including stainless steel (SS), 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, respectively (Figure S3). In addition, when Mg metal was

used as a working electrode, as shown in Figure S3D, the Mg plating/stripping on the surface of Mg metal was extremely smooth, as no overpotential was observed.

Subsequently, a symmetric Mg|0.5M **Mg-FPB**|Mg cell was assembled to evaluate the long-term electrochemical performance of the **Mg-FPB** electrolyte as shown in Figure 3A and 3B. The symmetric cell was tested from 50 $\mu\text{A}/\text{cm}^2$ to 1.0 mA/cm^2 current density. At 50 $\mu\text{A}/\text{cm}^2$ current density, the polarization is lowered to 70 mV (vs. Mg), even the current density was increased to 1.0 mA/cm^2 , the polarization is still below 100 mV (ca. 90 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+} cation and enable fast electrochemical deposition and stripping process. The symmetric cell was further cycled at 0.1 mA/cm^2 for 500 hours, and demonstrated highly stable polarization (Figure 3B). The stable polarization during galvanostatic cycling demonstrates that, benefitted from the stable FPB anion, the **MgFPB** electrolyte has an excellent cathodic stability.

To investigate the beneficial effects of the chelating FPB ligand in the **Mg-FPB** over the monodendate ligand used in the reported $\text{Mg}[\text{B}(\text{HFIP})_4]_2$ electrolyte,¹⁸ we also conducted CV studies of $\text{Mg}[\text{B}(\text{HFIP})_4]_2$ under the same conditions (Figure S2). It was found that $\text{Mg}[\text{B}(\text{HFIP})_4]_2$ displayed a larger overpotential (267 mV) and lower coulombic efficiency (83%) for Mg deposition/stripping than **Mg-FPB** although comparable cathodic stability (see Table 1). The Mg deposition/stripping reversibility of the **Mg-FPB** electrolyte is much better than that of $\text{Mg}[\text{B}(\text{HFIP})_4]_2$ (Figure S2 and S4). Furthermore, in the symmetric cell studies, the $\text{Mg}[\text{B}(\text{HFIP})_4]_2$ electrolyte manifested much higher overpotential (Figure S5 and S6), which is consistent with the literature.¹⁸ The $\text{Mg}[\text{B}(\text{HFIP})_4]_2$ electrolyte took ca. 150 hours to reach comparable overpotential as **Mg-FPB**. In the bulky electrochemical Mg deposition studies, both **Mg-FPB** and $\text{Mg}[\text{B}(\text{HFIP})_4]_2$ electrolytes yielded a smooth and dendrite free Mg layer (Figure S7). However, in the EDX spectrum of Mg layer deposited from $\text{Mg}[\text{B}(\text{HFIP})_4]_2$, there were 12.5% C, 9.9% O, and 1.9% F elements. The observation indicates the electrochemical decomposition of the $[\text{B}(\text{HFIP})_4]^-$ anion during the Mg plating process. In contrast, the EDX spectrum of Mg layer deposited from **MgFPB** electrolyte was very clean, only Mg metal was observed.

In addition, the chemical stability of the **Mg-FPB** and $\text{Mg}[\text{B}(\text{HFIP})_4]_2$ electrolytes was further compared by exposure to moisture (1% water added). As shown in Figure S8, the **Mg-FPB** electrolyte remained a clean solution after water treatment for two days, and its ^{19}F -NMR spectrum remained unchanged, which indicated the high chemical stability of FPB anion against hydrolysis. However, the $\text{Mg}[\text{B}(\text{HFIP})_4]_2$ electrolyte was changed from clean solution to a white gel. A new signal at -76.45 ppm chemical shift was observed in the ^{19}F -NMR spectrum which clearly indicated the decomposition of the $[\text{B}(\text{HFIP})_4]^-$ anion. The observed superior electrochemical and chemical stability of **Mg-FPB** over $\text{Mg}[\text{B}(\text{HFIP})_4]_2$ is attributed to the stabilization effect of the perfluorinated pinacolato bidentate ligand. In addition, albeit subject to further mechanistic studies, we hypothesize that acidic proton in the alpha carbon of the HFIP substituent may be also responsible to the inferior performance of the $\text{Mg}[\text{B}(\text{HFIP})_4]_2$ 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 (> 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 2.0 V battery voltage and 150 mAh/g discharge capacity at a current density of 10 μ A/g. However, the Mg/MnO₂ battery using chlorides containing MMAC electrolyte was constantly charged at 1.1 V due to the lower anodic stability and corrosion of electrolyte to the SS current collector while delivering a negligible discharge capacity (Figure 4, red curves).

It is worth noting that, as the FPB counter anion delivers excellent chemical and electrochemical stabilities, the FPB-based alkaline or alkaline earth metal salts, including Li-FPB, Na-FPB, K-FPB, and Ca-FPB, were also prepared similarly. Li-FPB has demonstrated promising metal deposition electrochemistry in preliminary studies (Figure S10). These salts were expected to have broad applications in energy storage and other fields.

In conclusion, a new Cl-free Mg electrolyte with non-coordinating perfluorinated pinacolatoborate counter anions was developed and comprehensively studied by NMR, single crystal x-ray diffraction, and electrochemical studies. The **Mg-FPB** electrolyte exhibited outstanding electrochemical performance for Mg plating/stripping with overpotential of 197 mV, a coulombic efficiency of 95%, and 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. In addition, the molecular design of **Mg-FPB** electrolyte with the emphasis of the highly stable perfluorinated chelating ligands for the counter anion will inspire the development of new electrolytes not limited to Mg²⁺ ion.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(A) Synthesis of **Mg-FPB**. (B) and (C) ^{19}F and ^{11}B -NMR spectra of **Mg-FPB** in $\text{MeCN-}d_3$. (D) X-ray single crystal structure of DGM solvated **Mg-FPB**. Mg, green; O, red; C, gray; H, white; B, orange; F, green yellow.

Figure 2.

(A) CV curves of 0.5 M **Mg-FPB** electrolyte in DGM on glassy carbon working electrode. (B) LSV curves of different working electrodes shown the anodic stability of the **Mg-FPB** electrolyte in DGM: stainless steel (SS, blue), Ti (green), Al (purple), glassy carbon (GC, orange). Condition: Mg as reference and counter electrode, 50 mV/s scan rate.

Figure 3.

(A) Mg metal plating/stripping from an Mg|0.5 M **Mg-FPB**|Mg symmetric cell tested at current density from 50 $\mu\text{A}/\text{cm}^2$ to 1.0 mA/cm^2 . (B) Galvanostatic cycling performance of Mg|0.5 M **Mg-FPB**|Mg symmetric cell at 0.1 mA/cm^2 .

Figure 4.
The representative charge/discharge curves of Mg-MnO₂ battery using 0.5 M **Mg-FPB** electrolyte in DGM at 10 μ A/g current density.

Table 1.

Performance comparison of the 0.5 M Mg-FPB and Mg[B(HFIP)₄]₂ electrolytes in DGM.

Electrolyte	η (mV)	CE (%)	E_{anodic} (V, vs Mg)	Electrochemical stability	Chemical stability
Mg-FPB	197	95	4.0	no fluoride deposition	stable with moisture
Mg[B(HFIP) ₄] ₂	267	83	4.0	fluoride deposition	decompose with moisture