

Facile Room-Temperature Electrodeposition of Rare Earth Metals in a Fluorine-Free Task-Specific Electrolyte

August 2023

Changing the World's Energy Future

Yating Yuan, James Gaugler, Juntian Fan, Bishnu Prasad Thapaliya, Huimin Luo, Abderrahman Atifi, Luis A Diaz Aldana

DISCLAIMER

This information was prepared as an account of work sponsored by an agency of the U.S. Government. Neither the U.S. Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness, of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. References herein to any specific commercial product, process, or service by trade name, trade mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the U.S. Government or any agency thereof.

Facile Room-Temperature Electrodeposition of Rare Earth Metals in a Fluorine-Free Task-Specific Electrolyte

Yating Yuan, James Gaugler, Juntian Fan, Bishnu Prasad Thapaliya, Huimin Luo, Abderrahman Atifi, Luis A Diaz Aldana

August 2023

Idaho National Laboratory Idaho Falls, Idaho 83415

http://www.inl.gov

Prepared for the U.S. Department of Energy Under DOE Idaho Operations Office Contract DE-AC07-05ID14517

Facile Room-Temperature Electrodeposition of Rare Earth Metals in a Fluorine-Free Task-Specific Electrolyte

Yating Yuan, James Gaugler, Juntian Fan, Bishnu Prasad Thapaliya, Huimin Luo, Abderrahman Atifi, Luis A. Diaz, and Sheng Dai*



electrode. Raman spectroscopy of the electrolyte reveals a synergetic effect between rare earth borohydride and lithium borohydride which promotes the dissociation of both borohydride salts, resulting in significantly increased ionic conductivity and electrochemical performance. Cyclic voltammetry and in-depth X-ray photoelectron spectroscopy of the deposits suggest that the electrodeposition of rare earth metals could undergo a Li-mediated reduction process. Quantitative analysis of the deposits reveals that the overall concentration of the rare earth elements reaches 75% which contains 40-48% metallic phase.

KEYWORDS: rare earth elements, electrodeposition, passivation effect, neodymium, dysprosium

INTRODUCTION

Rare earth elements (REEs) are critical to modern civilization, and the demand is predicted to increase as the world transitions to a renewable energy economy.¹⁻³ Neodymium, a vital component of high-performance permanent magnets, is one of the most widely used REEs, and its annual global demand is over 135,000 tons.⁴ Due to the uneven geographic distribution of REE minerals, the supply of REEs is significantly dominated in only a few regions.⁵ To secure the supply chain and maximize the utilization of REEs, efforts should not only be focused on the production of REEs from mineral ores but also on secondary sources such as end-of-life products, both of which require an efficient reduction process to produce REE metals for the synthesis of new magnets. Currently, the leading technology for the production of REE metals is molten fluoride salt electrolysis, a highly energy intensive and environmentally deleterious process.^{6–8} Therefore, development of processing alternatives that can provide energy savings, without environmental impacts, such as room-temperature electrochemical deposition of REE metals, is of great interest.

eliminating the passivation effect, the deposition process exhibits a stable current and accumulates a thick neodymium deposit on the

Due to the high electropositivity of REE metals, a nonaqueous electrolyte with a wide electrochemical window is required for electrodeposition.^{9,10} Previous efforts have been focused on Fluorine (F)-containing systems, in particular, ionic liquids (ILs) and organic electrolytes containing bis(trifluoromethane)sulfonimide (TFSI) or trifluoromethanesulfonate anions.^{11–18} While the electrodeposition of various REE metals has been reported in these systems, the application of F-containing ILs has been greatly hindered by various obstacles. Among them is the so-called passivation effect which can significantly impede stable deposition.^{17,19,20} This effect likely originates from an electrically insulating layer formed by either coreduction of anions alongside the REE metal ions or decomposition of the organic solvent. This layer is likely a mixture of metal fluoride and metal organic compounds. The formation of this passivation layer is a general phenomenon that has been widely observed and studied in the electroplating processes of other highly electropositive metals (Li, Na, K, Ca, and Mg).^{21–27} While this passivation layer has proven beneficial in battery applications for

Received: March 15, 2023 Revised: July 30, 2023 Published: August 17, 2023





single-valent light elements (e.g., Li and Na), it is detrimental for metal deposition. Multivalent metals (e.g., Ca, Mg, and REE metals) with large radii are not able to diffuse through this insulating layer, resulting in a significantly retarded reduction current or large overpotential for deposition and stripping.^{17,19,21–23,26} Additionally, this passivation layer introduces impurities into the product and lowers the current efficiency by introducing parasitic side reactions. This effect has been widely investigated in the electroplating of divalent metals (Mg and Ca) in F-based electrolytes, but little attention has been paid to this topic in relation to the electrodeposition of trivalent REE metals.^{24–27} Except for the passivation effect, pricey precursors that are needed to synthesize F-containing ILs which make them less economically competitive.

The solvation structure of the metal ion is often reported as a major determining factor of its electrochemical reduction pathway and is thus critical in minimizing the passivation effect.²⁷⁻³⁰ In tuning the solvation structure, the strength of the electrostatic interaction between the metal ion and the ligand must be balanced to minimize parasitic reactions. If the metal ion is strongly bound by the ligand, the desolvation process will be energetically costly and result in a high electrodeposition overpotential and decomposition of the ligand.^{27,28,31} On the other hand, if the metal ion is poorly solvated, the formation of contact ion pairs will reduce the solution's conductivity and, in this case, generate metal fluorides by coreduction of F-based anions at the cathode.²⁷ Due to the high charge density of REE metal ions, the electrode passivation of REEs is severe. Therefore, the design and investigation of suitable ligands for REE electrodeposition requires systematic experimentation and theoretical guidance.

A straightforward approach to eliminate the passivation effect is the development of F-free systems. Previous studies have demonstrated the successful electrodeposition of divalent Mg and Ca metals from borohydride and monocarborane anionbased systems.^{32–35} However, few reports of this approach exist for REE electrodeposition. Recently, dicyanamide ([DCA]⁻) anion-based ionic liquids were reported as an F-free medium for REE deposition.^{20,36} Xu reported that in 1-ethyl-3-methylimidizolium dicyanamide ([EMIM][DCA]) IL, with NdCl₃ as the Nd precursor, Nd³⁺ cannot be reduced independently but can be codeposited with Fe²⁺ to form Nd-Fe alloy.³⁶ Later, Periyapperuma reported the electrodeposition of Nd using hydrated neodymium nitrate in N-butyl-N-methylpyrrolidinium dicyanamide ($[C_4mpyr][DCA]$) IL.²⁰ XPS results confirmed the deposition of metallic Nd accompanied by Nd₂O₃ due to the presence of H₂O in the system. Another attempt was made with a chloride-based organic electrolyte by adding Nd₂Cl₆(DME)₄ to 4 equiv of LiBH₄ in MeTHF.¹⁷ The deposition current lasted longer than the control experiment containing TFSI anionbased salt, which suggests that the passivation effect originating from the F-containing anion was suppressed on its absence. However, approximately 1:1 Nd:Cl mole ratio was found in the final product, which could be due to the formation of reduced REE- Cl_x clusters. Therefore, it is necessary to continue searching for systems that can produce high purity REE metals without electrode passivation. Inspired by pioneering work in the electrodeposition of Mg and Ca from borohydride salts, we demonstrate that a borohydride-based system is a promising candidate for room-temperature REE electrodeposition.^{33,34} In addition to avoiding the passivation effect, this borohydride system may also be economically competitive since the borohydride precursor (e.g., $NaBH_4$) has been produced at

the industrial scale with a much lower price than the currently commercial available F-containing precursors,³⁷

In this work, we synthesized REE borohydride salts from REE chloride and LiBH₄ by using a mechanochemical metathesis reaction and investigated the effects of ethyl ether (EE) and dimethyl sulfide (MS) as solvents for the electrochemical deposition of REE metals (Nd and Dy). The REE borohydride-based electrolyte was characterized by cyclic voltammetry (CV), chronoamperometry, and Raman spectroscopy. The obtained deposits were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), inductively coupled plasma optical emission spectroscopy (ICP-OES), and X-ray photoelectron spectroscopy (XPS). Experimental results indicate that the proposed borohydride-based electrolyte can effectively eliminate passivation effect and subsequently produce deposits with high rare earth content.

MATERIALS AND METHODS

Chemicals and Materials. Anhydrous $NdCl_3$ (99.9%), anhydrous $DyCl_3$ (99.9%), LiBH₄ (95%), Tris[*N,N*-bis(trimethylsilyl)amide]neodymium (98%), ethyl ether, dimethyl sulfide (99%), boranedimethyl sulfide complex (94%), pentane, and tetrahydrofuran (THF) were all purchased from Thermo Scientific Chemicals and used without further purification.

Synthesis of Rare Earth Borohydride Electrolyte. The synthesis of rare earth borohydride was based on a mechanochemical driven metathesis reaction of REE chloride and LiBH₄. The synthesis was performed in an MTI MSK-SFM-3 high-speed ball miller under argon in an 80 mL stainless-steel jar and beads (diameter 5 mm). The mole ratio between REE chloride (NdCl₃, DyCl₃) and LiBH₄ was 1:4. The ball milling was conducted for 15 min followed by 5-min break to prevent overheating. The total milling time was 2 h. After ball milling, the mixture was added into ethyl ether or dimethyl sulfide. The rare earth borohydride solution and the insoluble LiCl precipitate were separated by centrifugation. The concentration of the prepared electrolyte is 0.6 M. The solvent-free rare earth borohydride was obtained after the reaction mixture was dried at room temperature under vacuum for 2 h and then dried at 90 °C under vacuum for 2 h.

The synthesis of lithium-free rare earth borohydride was based on a previously reported method under an argon atmosphere.³⁸ Borane dimethyl sulfide (0.4 g, 0.0053 mol) was dissolved in dry pentane, and tris((hexamethyldisilyl)amido)neodymium (0.70 g, 0.001 mol) was added, which resulted in the immediate precipitation of neodymium borohydride. The mixture was stirred for 24 h and evaporated to dryness under vacuum. The solids were recrystallized from THF to yield Nd(BH₄)₃·1.5 THF (36% yield).

Electrochemistry of Rare Earth Borohydride Electrolyte. The electrochemistry of the rare earth borohydride electrolyte was studied in a custom three-electrode cell inside an argon-filled glovebox with oxygen and moisture level less than 1 ppm.CV and chronoamperometry were performed with a Reference 600 potentiostat without convection and Gamry instrument potentiostat with a Pt wire (1 mm in diameter) or Cu foil as the working electrode, Pt wire as the quasi reference electrode, and carbon paper as the counter electrode. The potential of redox peaks versus Ferrocene/ferrocenium (Fc/Fc^+) was calibrated by Fc/Fc^+ redox couple as the internal reference.

Material Characterizations. Powder X-ray diffraction (XRD) data were recorded with a PANalytical Empyrean diffractometer operated at 45 kV and 40 mA (scanning step: 0.02° per step). The diffraction patterns were recorded in the range of $10-80^{\circ}$. $\lambda = 0.1540598$ nm. XPS experiments were performed with a PHI 3056 spectrometer equipped with an Al anode source operated at 15 KV and an applied power of 350 W and a pass energy of 93.5 eV. Samples were mounted on a foil since the C 1s binding energy was used to calibrate the binding energy shifts of the sample (C 1s = 284.8 eV). SEM images and EDX mapping images were collected on a ZEISS AURIGA CROSSBEAM FIB scanning electron microscope. ICP-OES analysis was performed using an Agilent 5110 ICP-OES spectrometer. Raman spectroscopy was performed



Figure 1. (a) Schematic illustration of the synthesis process of the $Nd(BH_4)_3$ electrolyte. (b) XRD pattern of $Nd(BH_4)_3$ dried from $Nd(BH_4)_3$ -EE solution. (c) XRD pattern of the precipitate.



Figure 2. (a) CV curve of Nd(BH₄)₃-EE; working electrode: Pt wire. (b) CV curve of LiBH₄ in ethyl ether. (c) CV curve of pure-Nd(BH₄)₃-EE. (d) Current-time curve of chronoamperometry of Nd(BH₄)₃-EE electrolyte at -3.2 V vs Fc/Fc⁺; working electrode: Pt wire (inset: photo of deposits on the working electrode).

using a Renishaw In-Via Raman spectrum instrument with an emission laser wavelength of 532 nm.

RESULTS AND DISCUSSION

The mechanochemical synthesis of REE borohydrides is driven by an efficient solid-state metathesis reaction between an REE chloride and LiBH₄. This method avoids the high-pressure synthesis of REE hydride precursors and exhibits a much faster reaction rate than solution-phase metathesis reactions.³⁹⁻⁴¹ Figure 1a illustrates the synthesis procedures of $Nd(BH_4)_3$ solution. After ball milling NdCl₃ with LiBH₄, the mixture was added into ethyl ether. Ethyl ether was chosen as the solvent due to its electrochemical stability, good solubility for REE borohydrides, and low solubility for LiCl.^{41,42} Upon addition of the mixture to ethyl ether, $Nd(BH_4)_3$ is dissolved leaving a white precipitate (Figure 1a), which was confirmed as LiCl by the XRD pattern (Figure 1c). Because an excess of LiBH₄ to NdCl₃ was used during the mechanochemical synthesis process, the presence of Li in the electrolyte was confirmed by ICP-OES, with a mole ratio of 1:3 between Li and Nd. The upper purple supernatant was separated and dried under vacuum and confirmed as Nd(BH₄)₃ by XRD as well (Figure 1b).^{43,44}

This ethyl ether-based $Nd(BH_4)_3$ electrolyte $[Nd(BH_4)_3-EE]$ was studied by CV before performing electrodeposition. In Figure 2a, the CV curve of the prepared $Nd(BH_4)_3$ -EE electrolyte exhibits one pair of reversible redox peaks located at -2.9 V vs Fc/Fc⁺. These peaks cannot be directly assigned to Nd³⁺/Nd redox due to the presence of excess LiBH₄ in the electrolyte. The high reversibility of the observed redox peaks suggests that the peaks are due to Li/Li⁺ as all other reported instances of low-temperature REE electrodeposition show irreversibility for REE electrodeposition.11-17,20,36 However, the position of these peaks deviates significantly from the literature value for Li/Li⁺ vs Fc/Fc⁺, which is typically between 3.3 and 3.7 V. 45,46 It is possible that the positive shift of Li/Li⁺ vs Fc/Fc^+ could arise from the effect of the solvation energy; however, such a shift is only ~0.3 V based on previous literature reports.⁴⁶ In order to gain more understanding of this peak, control experiments were performed by studying the CV curve of a lithium-free $Nd(BH_4)_3$ -EE solution (denoted as pure- $Nd(BH_4)_3$ -EE) and a neodymium-free LiBH₄-EE solution. Lithium-free $Nd(BH_4)_3$ was synthesized via the reaction between neodymium silylamide and borane-dimethyl sulfide. XRD pattern (Figure S1 see Supporting Information (SI)) of the lithium-free $Nd(BH_4)_3$ is in agreement with the literature and confirmed to be Nd(BH₄)₃·1.5 THF.⁴⁴ ICP-OES analysis of this product indicated the absence of alkaline impurities below the detection limit of a 0.7% mole ratio. However, to our surprise, both the pure-Nd $(BH_4)_3$ -EE solution and the LiBH₄-EE solution were not electrochemically active (Figure 2b,c), despite both two borohydride salts being soluble in ethyl ether (\sim 3 g of LiBH₄ can be dissolved in 100 g of ethyl ether at room temperature).⁴⁷ The inactive lithium-free pure-Nd(BH₄)₃-EE solution likely originates from the covalent nature of the Nd-BH₄ bond, which cannot provide sufficient conductivity because of the inefficient dissociation of $Nd(BH_4)_3$ into ions.⁴⁸ The ionic conductivity of ethyl ether-based electrolyte was measured and listed in Table S1. The simultaneous presence of LiBH₄ and $Nd(BH_4)_3$ in $Nd(BH_4)_3$ -EE yields a significantly enhanced ionic conductivity, indicating that there is a synergetic effect between $LiBH_4$ and $Nd(BH_4)_3$ which was investigated by Raman spectroscopy.

Raman spectroscopy of ethyl ether-based electrolytes was studied to gain further understanding of the electrolyte speciation. Figure S2 shows the Raman spectra obtained from pure ethyl ether, LiBH₄-EE, Nd(BH₄)₃-EE, and Dy(BH₄)₃-EE solution. Figure S2a shows ethyl ether mode around 840 cm⁻¹ which is ascribed to the C–O skeleton stretching and the methyl group rocking of the ethyl ether.⁴⁹ The splitting of the peak into a doublet with a main peak at 846 cm^{-1} and a shoulder peak at 837 cm⁻¹ is attributed to the presence of TT and TG conformers of ethyl ether.⁴⁹ The C–O stretching mode of ether is usually sensitive to the local environment and is a good indicator of coordination, and hence it is utilized here to study borohydride solutions. An increase in the relative intensity of the TG peak can be observed for all boron hydride containing ethyl ether solutions, indicating an increased population of TG conformers. This is likely due to the coordination of ethyl ether to Li^+ , Nd^{3+} , or Dy³⁺ ions since TG conformer is more sterically conducive to coordination with cations through oxygen. The Raman peaks in the 2050–2550 cm⁻¹ region in Figure S2b are ascribed to B–H vibrations which reveal the anionic features of ethyl ether-based solutions. For LiBH₄-EE solution, a doublet can be found at 2250 and 2375 cm⁻¹ which was attributed to the presence of aggregates rather than fully dissociated free ions, as evidenced by its extremely low ionic conductivity ($<0.001 \text{ mS cm}^{-1}$).⁵⁰ For $Nd(BH_4)_3$ -EE and $Dy(BH_4)_3$ -EE solution, the spectra are composed of three peaks at 2137, 2214, and 2467 cm⁻¹ which can be assigned to ionic $(BH_4)^-$ (or free $(BH_4)^-$), bridging B- $H_{bridging}$, and terminal B- $H_{terminal}$ vibrations.^{48,51,52} This suggests the coexistence of anion-coordinated ion pairs and free $(BH_4)^$ anions in REE borohydride-ethyl ether solution. The absence of peaks at 2250 and 2375 cm⁻¹ suggests that $REE(BH_4)_3$ can promote the dissociation of LiBH₄ and contribute to higher ionic conductivity of REE(BH₄)₃-EE solutions, likely via a synergetic mechanism. Based on these results, the possible active species in REE-EE solutions are assumed to be REE³⁺, Li⁺, [REE $(EE)_{n}$ $(BH_{4})_{m}$ $]^{(3-m)_{+}}$, $[LiREE (EE)_{n} (BH_{4})_{m}]^{(4-m)_{+}}$, and $(BH_4)^-$.

Based on these CV results on the mechanochemically synthesized $Nd(BH_4)_3$ -EE solution, REE electrodeposition was performed by chronoamperometry at -3.2 V vs Fc/Fc⁺ for 10 h using a Pt wire as the cathode (Figure 2d). The deposition current density remained above 1 mA/cm^2 for the initial 3 h and decreased slowly over the remaining 7 h. In contrast, previously reported F-containing systems undergo rapid decay to a negligible current within minutes.^{17,19} After 10 h of deposition, accumulation of a thick black deposit on the Pt wire cathode was observed (Figure 2d inset). These observations suggest the successful elimination of the passivation effect in this F-free borohydride system. The deposited product is not stable in air and readily reacts with moisture as it quickly converts to a light purple powder within seconds upon exposure to air. The same procedure used for Nd metal production was applied to prepare $Dy(BH_4)_3$ -EE solution and perform electrodeposition. As expected, XRD confirmed the formation of $Dy(BH_4)_3$ from the metathesis reaction between $DyCl_3$ and $LiBH_4$ (Figure S3). The $Dy(BH_4)_3$ -EE solution exhibited similar electrochemical characteristics as Nd(BH₄)₃-EE system (Figure S4), which suggest that this F-free electrodeposition method can be applied to other trivalent REEs.

The morphology and composition of the electrodeposited Nd and Dy samples were characterized by SEM, EDX, and ICP-OES. The Nd sample is composed of dense aggregates (Figure



Figure 3. (a) SEM and EDX mapping of the deposited Nd sample from $Nd(BH_4)_3$ -EE solution. (b) EDX spectrum of the Nd sample from $Nd(BH_4)_3$ -EE solution.

3a), while the Dy sample is relatively loose and composed of dispersed particles (Figure S5). The EDX spectra (Figures 3b and S5b) confirms the presence of Nd and Dy in the deposits. Intense signals of Cl and O were also observed for both samples. The presence of O is likely due to oxidation by O_2 and H_2O due

Table 1. EDX Analysis of Nd Sample from $Nd(BH_4)_3$ -EE Solution

Nd sample from $Nd(BH_4)_3$ -EE solution	mass %
Nd	58.5
Cl	33.8
0	7.7

to short air exposure during sample preparation or electrochemical decomposition of the electrolyte. The elemental mappings are displayed in Figures 3a and S5a to provide direct evidence of the dispersion of Nd and Dy. The determination of Li and B was not performed by EDX due to its inability to detect light elements. Based on the EDX analysis, the weight percent composition of the samples is listed in Tables 1 and S2. The weight percentages of Nd and Dy were determined to be 58.5 and 55.2%, accompanied by a significant amount of Cl (over 30%). The Cl impurity in these deposits was also observed in previously studied borohydride systems.¹⁷ However, the formation mechanism could be different because majority of Cl⁻ was precipitated as insoluble LiCl in our synthesis, whereas all of Cl⁻ exists as soluble species in the previous Nd₂Cl₆(DME)₄-LiBH₄ system.¹⁷ The high Cl content is unlikely to originate from solvated LiCl or NdCl₃ as both of them have very low solubility in ethyl ether. Rather, it is likely due to the formation of Cl-containing complex, for example, the $LiRE(BH_4)_3Cl$ complex, which is reported to form during the

Table 2. ICP-OES Analysis of Nd Sample Obtained from $Nd(BH_4)_3$ -EE Solution

Nd sample from $Nd(BH_4)_3$ -EE solution	mass %
Nd	61
В	13
Li	1
O + Cl + others	25

ball milling or heating.⁵³ Interestingly, chlorine does not feature any passivation unlike its neighboring halogen fluorine, and it is reported that Cl can act as a depassivating agent in the electrodeposition of Mg.⁵⁴

In order to more precisely quantify the REE content, the Nd sample was analyzed by ICP-OES, and the results are listed in Table 2. Based on the whole weight of the sample, Nd

concentration is about 61%, which is consistent with EDX results. The lithium concentration is only 1 wt %, which is lower than the ratio (10 wt %) in the electrolyte. By combining CV and ICP results, the electrodeposition of Nd is presumed to be Limediated reduction of Nd.

While the $REE(BH_4)_3$ -ethyl ether solution can produce deposits with reasonably high REE content via passivation-free electrodeposition, Cl contamination remains a major problem. In order to eliminate Cl, dimethyl sulfide, which has been reported as an extractive solvent in the synthesis of halide free REE borohydride, was utilized as a solvent to replace ethyl ether.⁴³

The use of dimethyl sulfide as a solvent for the REE metathesis mixture yielded a pink $Nd(BH_4)_3$ solution with an insoluble white LiCl precipitate (Figure 4a inset). In Figure 4a, CV of $Nd(BH_4)_3$ -dimethyl sulfide $[Nd(BH_4)_3$ -MS] solution shows one pair of redox peaks with a less reversible shape than the $Nd(BH_4)_3$ -EE solution, which indicates a shift toward predominance of Nd reduction in the $Nd(BH_4)_3$ -MS solution. Similar to the $Nd(BH_4)_3$ -EE solution, the LiBH_4-MS and pure- $Nd(BH_4)_3$ -MS solution exhibited no electroactivity (Figure S6). In Table S3, the ionic conductivity of methyl sulfide-based electrolytes follows a similar trend as ethyl ether-based solution, indicating the existence of a synergetic effect.

The speciation of dimethyl sulfide-based electrolyte was investigated by Raman spectroscopy. Figure S7 shows the Raman spectra of Nd(BH₄)₃-MS, pure-Nd(BH₄)₃-MS, and $Dy(BH_4)_3$ -MS electrolytes at 720-760 cm⁻¹ and 2050-2550 cm^{-1} regions, which correspond to the C–S asymmetric stretching of dimethyl sulfide and the B-H stretching of $(BH_4)^-$, respectively.⁵⁵ A shift of the C–S stretching mode from 744.2 cm⁻¹ (for pure dimethyl sulfide) to 742.6 cm⁻¹ [for $REE(BH_4)_3$ in dimethyl sulfide] could be ascribed to the coordination of dimethyl sulfide to REE cations which involves the change of C–S bond length induced by charge transfer between sulfur and REE^{3+} .^{56–58} The B–H stretching mode of the REE containing dimethyl sulfide solution in Figure S7b exhibits a similar pattern to the ethyl ether-based solutions which feature the coexistence of anion-coordinated ion pairs and free $(BH_4)^-$ anions and indicates the partial dissociation of $REE(BH_4)_3$ in dimethyl sulfide. The additional peak located at 2361 cm^{-1} suggests the formation of a different complex. It is worth noting that pure $Nd(BH_4)_3$ -MS displays a low intensity at 2221 cm⁻¹, indicating that only a low ratio of ionic (BH₄)⁻ can be formed without LiBH4 present in solution, which consequently results in a low ionic conductivity. However, the significant enhancement of 2221 cm⁻¹ peak can be observed in the Li-containing $REE(BH_4)_3$ -MS solution. This suggests that the presence of Li can facilitate the disassociation of $REE(BH_4)_3$, thereby improving the ionic conductivity and electrodeposition performance. This observation is similar to that of ethyl etherbased solutions, confirming the synergetic effect in dimethyl sulfide solutions. Based on the above results, we assume the electroactive species in the REE $(BH_4)_3$ -MS solution could be REE³⁺, Li⁺, [REE (MS)_n (BH₄)_m]^{(3-m)+}, [LiREE (MS)_n (BH₄)_m]^{(4-m)+}, and (BH₄)⁻.

The electrodeposition in Nd(BH₄)₃-MS solution was carried out potentiostatically at -3.5 V using copper film as the working electrode. The chronoamperogram (Figure 4b) exhibited a stable current density for 10 h and suggests a passivation-free electrodeposition mechanism. After deposition, the black deposit on the Cu film (Figure 4b inset) was recovered and characterized by SEM, EDX, and ICP-OES. The obtained Nd



Figure 4. (a) CV of $Nd(BH_4)_3$ -MS solution; inset: photo of $Nd(BH_4)_3$ -MS solution with insoluble LiCl at bottom. (b) Current-time curve of chronoamperometry at -3.5 V; inset: photo of the working electrode after electrodeposition. (c) SEM image of the Nd sample obtained from $Nd(BH_4)_3$ -MS solution. (d) EDX spectrum of the Nd sample obtained from $Nd(BH_4)_3$ -MS solution.

Table 3. EDX Analysis of Nd Sample Obtained from Nd(BH₄)₃-MS Solution

Nd sample from $Nd(BH_4)_3$ -MS solution	mass %
Nd	75.2
Cl	2.3
S	3
0	19.5

deposit shows a dense packed filmlike morphology (Figure 4c), similar to the Nd sample from $Nd(BH_4)_3$ -EE solution. The EDX spectrum (Figure 4d) shows characteristic Nd peaks and significantly suppressed Cl peaks. The elemental composition based on EDX is provided in Table 3, which shows a nearly 17% increase of Nd from 58.5 to 75.2%, more importantly, more than

Table 4. ICP-OES Analysis of Nd Sample Obtained from $Nd(BH_4)_3$ -MS Solution

Nd sample from $Nd(BH_4)_3$ -MS solution	mass %
Nd	75
В	7
Li	1
O + Cl + S + others	17

10-fold decrease of Cl from 33.8 to 2.3%, compared with ethyl ether solution. The slightly higher O level in the sample can be attributed to air exposure during EDX sample preparation. The presence of 3% sulfur indicates a small extent of solvent decomposition during the electrodeposition. The EDX mapping images in Figure S8 show the distribution of Nd, Cl, O, and S in the Nd sample. Quantitative analysis by ICP-OES (Table 4) indicates an elemental composition of Nd, B, and Li at 75, 7, and 1%, respectively. Similar compositional results were obtained for the Dy sample, as shown in Table S4. It is worth mentioning that

both deposits can generate sparks when directly contacted with water, which is an indicator of extremely high reactivity of metallic REE material. Such a high reactivity has also been previously observed on nanosized rare earth metal particles that are chemically reduced by lithium naphthalenide in ether solution.⁵⁹

The in-depth XPS analysis was carried out to gain additional insight into the chemical state of deposited REE samples. Figure 5a,c shows the $3d_{5/2}$ spectra of Nd obtained from Nd(BH₄)₃-EE and $Nd(BH_4)_3$ -MS. Both spectra can be deconvoluted into a main peak at 983 eV and a satellite peak at 978 eV, which can be assigned to the oxidized Nd and metallic Nd, respectively.⁶⁰ Argon sputtering was performed for 10 min to remove the surface layer of the samples in order to analyze the middle layer. A slightly enhanced 978 eV peak was observed for both Nd samples after sputtering, indicating a higher concentration of Nd metal in the middle layer. However, the 983 eV peak remains dominant which suggests that the oxidation of Nd is primarily derived from the reaction of newly deposited Nd with O or S containing species in the electrolyte (e.g., solvent) rather than the oxidation by air or moisture during the postdeposition treatment. Based on the sputter-etched XPS spectra, the percentage of metallic Nd and oxidized Nd was calculated to be 43.3 and 56.7% [for sample from Nd(BH₄)₃-EE] and 48.3 and 51.7% [for sample from $Nd(BH_4)_3$ -MS], respectively. The survey of spectra in Figure S9 shows the presence of Li, O, and Cl for sample from Nd(BH_{4})₃-EE and Li, O, Cl, and S for sample from $Nd(BH_4)_3$ -EE, which is consistent with the EDX results. In particular, the high-resolution Li 1s spectra was analyzed and displayed in Figure S10 to study the chemical state. For the $Nd(BH_4)_3$ -EE sample, there is a shift of Li 1s peak to lower binding energy after etching, indicating a change of average chemical state from oxide to metallic, which confirms the coreduction of Li. The obvious intensity decrease of Li 1s after

pubs.acs.org/journal/ascecg



Figure 5. In-depth XPS spectra of Nd and Dy samples: (a) Nd sample obtained from Nd(BH₄)₃-EE, (b) Dy sample obtained from Dy(BH₄)₃-EE, (c) Nd sample obtained from Nd(BH₄)₃-MS, and (d) Dy sample obtained from Dy(BH₄)₃-MS.

etching reveals a lower concentration of Li inside the sample. This could be explained by the Li-mediated reduction mechanism since the codeposited Li at the earlier stage could be continuously consumed through the chemical reduction reaction with Nd^{3+} . Figure 5b,d shows the $3d_{5/2}$ spectra of Dy. The deconvoluted spectra of etched samples display two peaks at 1294.5 and 1297 eV which could be assigned to metallic Dy and oxidized Dy.⁶⁰ Similar to the Nd case, the oxidized Dy likely originated from the chemical or electrochemical reaction with O or S containing species inside the solvent. The ratio of metallic Dy to oxidized Dy was calculated to be 42.1 and 57.9% [for sample from $Dy(BH_4)_3$ -EE] and 42.4 and 57.6% [for sample from $Dy(BH_4)_3$ -MS]. The Li 1s spectra of Dy samples also exhibit an intensity decrease after sputtering, suggesting Limediated reduction mechanism. These XPS analyses suggest that metallic Nd and Dy were successfully deposited from ethyl ether and methyl sulfide solutions.

CONCLUSIONS

We have developed a passivation-free system for the electrodeposition of rare earth metals. $Nd(BH_4)_3$ and $Dy(BH_4)_3$ salts were first synthesized by a mechanochemically driven metathesis reaction between REE chloride and LiBH₄. These borohydride salts were then dissolved in ethyl ether or dimethyl sulfide, and their electrochemical properties were studied by Raman spectroscopy, CV, and chronoamperometry. Evidence was found for a synergetic effect between REE borohydride and LiBH₄ which can promote the dissociation of borohydride salts and facilitate the electrochemical properties. Combined with the in-depth XPS analysis of deposits, the reduction mechanism of these rare earth metals likely proceeds through a coreduction or Li-mediated reduction pathway. Passivation-free electrodeposition can be performed in both ethyl ether and dimethyl sulfide; however, the product obtained from the dimethyl sulfide solvent exhibits superior purity and suppresses Cl contamination by preventing the formation of Cl-containing complexes. XPS, EDX, and ICP-OES analyses of the deposits indicate that the overall concentration of the REEs reach 75% which contains 40–48% metallic phase.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.3c01519.

XRD, EDX, ICP-OES, and XPS results of the samples obtained from ethyl ether and dimethyl sulfide-based electrolyte; Raman spectra; CV of LiBH4 in dimethyl sulfide and pure-Nd(BH4)3-MS solution; ionic conductivity of LiBH4 and REE borohydride in dimethyl sulfide solution; and current efficiency of ethyl ether and dimethyl sulfide-based electrolyte (PDF)

AUTHOR INFORMATION

Corresponding Author

Sheng Dai – Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996, United States; Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States; orcid.org/ 0000-0002-8046-3931; Email: dais@ornl.gov

Authors

Yating Yuan – Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996, United States; Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

- James Gaugler Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996, United States
- Juntian Fan Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996, United States
- Bishnu Prasad Thapaliya Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States; © orcid.org/0000-0002-1697-0509
- Huimin Luo Manufacturing Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States; o orcid.org/0000-0003-1840-3716
- Abderrahman Atifi Chemical Systems Department, Idaho National Laboratory, Idaho Falls, Idaho 83415, United States; © orcid.org/0000-0002-0163-5660
- Luis A. Diaz Chemical Separations Department, Idaho National Laboratory, Idaho Falls, Idaho 83402, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acssuschemeng.3c01519

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Critical Materials Institute, an Energy Innovation Hub funded by the US Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Materials and Manufacturing Technologies Office under grant AL-12-350-001.

REFERENCES

(1) Dang, D. H.; Thompson, K. A.; Ma, L.; Nguyen, H. Q.; Luu, S. T.; Duong, M. T. N.; Kernaghan, A. Toward the Circular Economy of Rare Earth Elements: A Review of Abundance, Extraction, Applications, and Environmental Impacts. *Arch. Environ. Contam. Toxicol.* **2021**, *81*, 521– 530.

(2) Dushyantha, N.; Batapola, N.; Ilankoon, I. M. S. K.; Rohitha, S.; Premasiri, R.; Abeysinghe, B.; Ratnayake, N.; Dissanayake, K. The story of rare earth elements (REEs): Occurrences, global distribution, genesis, geology, mineralogy and global production. *Ore Geol. Rev.* **2020**, *122*, No. 103521.

(3) Balaram, V. Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. *Geosci. Front.* **2019**, *10*, 1285–1303.

(4) Junne, T.; Wulff, N.; Breyer, C.; Naegler, T. Critical materials in global low-carbon energy scenarios: The case for neodymium, dysprosium, lithium, and cobalt. *Energy* **2020**, *211*, No. 118532.

(5) Mancheri, N. A.; Sprecher, B.; Bailey, G.; Ge, J.; Tukker, A. Effect of Chinese policies on rare earth supply chain resilience. *Resour. Conserv. Recycl.* **2019**, *142*, 101–112.

(6) Zhu, H., Rare Earth Metal Production by Molten Salt Electrolysis. In *Encyclopedia of Applied Electrochemistry*, Kreysa, G.; Ota, K.-I.; Savinell, R. F., Eds.; Springer New York: New York, NY, 2014; 1765– 1772.

(7) Talens Peiró, L.; Villalba Méndez, G. Material and Energy Requirement for Rare Earth Production. JOM 2013, 65, 1327–1340. (8) Rush, R. G.; Taylor, P. R. In Rare Earth Reduction: A Technological Overview of State-of-the-Art Technology and Novel Developments, New Directions in Mineral Processing, Extractive Metallurgy, Recycling and Waste Minimization, Cham, 2023//; Reddy, R. G.; Anderson, A.; Anderson, C. G.; Fleuriault, C.; Spiller, E. D.; Strauss, M.; Vidal, E. E.; Zhang, M., Eds.; Springer Nature Switzerland: Cham, 2023; 393–417. (9) Zhou, J.; Meng, X.; Zhang, R.; Liu, H.; Liu, Z. Progress on Electrodeposition of Rare Earth Metals and Their Alloys. *Electrocatalysis* **2021**, *12*, 628–640.

(10) Simka, W.; Puszczyk, D.; Nawrat, G. Electrodeposition of metals from non-aqueous solutions. *Electrochim. Acta* **2009**, *54*, 5307–5319.

(11) Kazama, R.; Matsumiya, M.; Tsuda, N.; Tsunashima, K. Electrochemical analysis of diffusion behavior and nucleation mechanism for Dy(II) and Dy(III) in phosphonium-based ionic liquids. *Electrochim. Acta* **2013**, *113*, 269–279.

(12) Kondo, H.; Matsumiya, M.; Tsunashima, K.; Kodama, S. Attempts to the electrodeposition of Nd from ionic liquids at elevated temperatures. *Electrochim. Acta* **2012**, *66*, 313–319.

(13) Zhang, B.; Wang, L.; Pan, K.; Zhang, W.; Liu, Y.; Zhang, Y.; Zhang, L.; Shi, Z. LiNO3-Supported Electrodeposition of Metallic Nd from Nd-Containing Solvate Ionic Liquid. *J. Phys. Chem. C* 2021, *125*, 20798–20805.

(14) Orme, K.; Baek, D. L.; Fox, R. V.; Atifi, A. Water Interplays during Dysprosium Electrodeposition in Pyrrolidinium Ionic Liquid: Deconvoluting the Pros and Cons for Rare Earth Metallization. *ACS Sustainable Chem. Eng.* **2021**, *9*, 14631–14643.

(15) Bourbos, E.; Giannopoulou, I.; Karantonis, A.; Paspaliaris, I.; Panias, D. Reduction of Light Rare Earths and a Proposed Process for Nd Electrorecovery Based on Ionic Liquids. *J. Sustain. Metall.* **2018**, *4*, 395–406.

(16) Glukhov, L. M.; Greish, A. A.; Kustov, L. M. Electrodeposition of rare earth metals Y, Gd, Yb in ionic liquids. *Russ. J. Phys. Chem. A* **2010**, *84*, 104–108.

(17) Geysens, P.; Lin, P.-C.; Fransaer, J.; Binnemans, K. Electrodeposition of neodymium and dysprosium from organic electrolytes. *Phys. Chem. Chem. Phys.* **2021**, *23*, 9070–9079.

(18) Atifi, A.; Baek, D. L.; Fox, R. V. Electrodeposition of Dysprosium in pyrrolidinium triflate ionic liquid at ambient temperature: Unraveling system efficiency and impact of solvation interplays on the reduction process. *Electrochim. Acta* **2021**, *378*, No. 138140.

(19) Lodermeyer, J.; Multerer, M.; Zistler, M.; Jordan, S.; Gores, H. J.; Kipferl, W.; Diaconu, E.; Sperl, M.; Bayreuther, G. Electroplating of Dysprosium, Electrochemical Investigations, and Study of Magnetic Properties. J. Electrochem. Soc. **2006**, 153, C242.

(20) Periyapperuma, K.; Pringle, J. M.; Sanchez-Cupido, L.; Forsyth, M.; Pozo-Gonzalo, C. Fluorine-free ionic liquid electrolytes for sustainable neodymium recovery using an electrochemical approach. *Green Chem.* **2021**, *23*, 3410–3419.

(21) Bao, C.; Wang, B.; Liu, P.; Wu, H.; Zhou, Y.; Wang, D.; Liu, H.; Dou, S. Solid Electrolyte Interphases on Sodium Metal Anodes. *Adv. Funct. Mater.* **2020**, *30*, No. 2004891.

(22) Cheng, X.-B.; Zhang, R.; Zhao, C.-Z.; Wei, F.; Zhang, J.-G.; Zhang, Q. A Review of Solid Electrolyte Interphases on Lithium Metal Anode. *Adv. Sci.* **2016**, *3*, No. 1500213.

(23) Liu, W.; Liu, P.; Mitlin, D. Review of Emerging Concepts in SEI Analysis and Artificial SEI Membranes for Lithium, Sodium, and Potassium Metal Battery Anodes. *Adv. Energy Mater.* **2020**, *10*, No. 2002297.

(24) Forero-Saboya, J.; Davoisne, C.; Dedryvère, R.; Yousef, I.; Canepa, P.; Ponrouch, A. Understanding the nature of the passivation layer enabling reversible calcium plating. *Energy Environ. Sci.* **2020**, *13*, 3423–3431.

(25) Kuwata, H.; Matsui, M.; Imanishi, N. Passivation Layer Formation of Magnesium Metal Negative Electrodes for Rechargeable Magnesium Batteries. *J. Electrochem. Soc.* **2017**, *164*, A3229.

(26) Zhang, J.; Liu, J.; Wang, M.; Zhang, Z.; Zhou, Z.; Chen, X.; Du, A.; Dong, S.; Li, Z.; Li, G.; Cui, G. The origin of anode–electrolyte interfacial passivation in rechargeable Mg-metal batteries. *Energy Environ. Sci.* **2023**, *16*, 1111–1124.

(27) Rajput, N. N.; Qu, X.; Sa, N.; Burrell, A. K.; Persson, K. A. The Coupling between Stability and Ion Pair Formation in Magnesium Electrolytes from First-Principles Quantum Mechanics and Classical Molecular Dynamics. *J. Am. Chem. Soc.* **2015**, *137*, 3411–3420.

(28) Hou, S.; Ji, X.; Gaskell, K.; Wang, P.-F.; Wang, L.; Xu, J.; Sun, R.; Borodin, O.; Wang, C. Solvation sheath reorganization enables divalent metal batteries with fast interfacial charge transfer kinetics. *Science* **2021**, 374, 172–178.

(29) Melemed, A. M.; Skiba, D. A.; Gallant, B. M. Toggling Calcium Plating Activity and Reversibility through Modulation of Ca2+ Speciation in Borohydride-Based Electrolytes. *J. Phys. Chem. C* 2022, *126*, 892–902.

(30) Zhao, W.; Pan, Z.; Zhang, Y.; Liu, Y.; Dou, H.; Shi, Y.; Zuo, Z.; Zhang, B.; Chen, J.; Zhao, X.; Yang, X. Tailoring Coordination in Conventional Ether-Based Electrolytes for Reversible Magnesium-Metal Anodes. *Angew. Chem., Int. Ed.* **2022**, *61*, No. e202205187.

(31) Hahn, N. T.; Driscoll, D. M.; Yu, Z.; Sterbinsky, G. E.; Cheng, L.; Balasubramanian, M.; Zavadil, K. R. Influence of Ether Solvent and Anion Coordination on Electrochemical Behavior in Calcium Battery Electrolytes. *ACS Appl. Energy Mater.* **2020**, *3*, 8437–8447.

(32) Shao, Y.; Liu, T.; Li, G.; Gu, M.; Nie, Z.; Engelhard, M.; Xiao, J.; Lv, D.; Wang, C.; Zhang, J.-G.; Liu, J. Coordination Chemistry in magnesium battery electrolytes: how ligands affect their performance. *Sci. Rep.* **2013**, *3*, 3130.

(33) Mohtadi, R.; Matsui, M.; Arthur, T. S.; Hwang, S.-J. Magnesium Borohydride: From Hydrogen Storage to Magnesium Battery. *Angew. Chem., Int. Ed.* **2012**, *51*, 9780–9783.

(34) Wang, D.; Gao, X.; Chen, Y.; Jin, L.; Kuss, C.; Bruce, P. G. Plating and stripping calcium in an organic electrolyte. *Nat. Mater.* **2018**, *17*, 16–20.

(35) Tutusaus, O.; Mohtadi, R.; Arthur, T. S.; Mizuno, F.; Nelson, E. G.; Sevryugina, Y. V. An Efficient Halogen-Free Electrolyte for Use in Rechargeable Magnesium Batteries. *Angew. Chem., Int. Ed.* **2015**, *54*, 7900–7904.

(36) Xu, X.; Sturm, S.; Zavasnik, J.; Rozman, K. Z. Electrodeposition of a Rare-Earth Iron Alloy from an Ionic-Liquid Electrolyte. *ChemElectroChem* **2019**, *6*, 2860–2869.

(37) Schlesinger, H. I.; Brown, H. C.; Finholt, A. E. The Preparation of Sodium Borohydride by the High Temperature Reaction of Sodium Hydride with Borate Esters1. *J. Am. Chem. Soc.* **1953**, *75*, 205–209.

(38) Andersen, R. A. Tris((hexamethyldisilyl)amido)uranium(III): preparation and coordination chemistry. *Inorg. Chem.* **1979**, *18*, 1507–1509.

(39) Grinderslev, J. B.; Møller, K. T.; Bremholm, M.; Jensen, T. R. Trends in Synthesis, Crystal Structure, and Thermal and Magnetic Properties of Rare-Earth Metal Borohydrides. *Inorg. Chem.* **2019**, *58*, 5503–5517.

(40) Paskevicius, M.; Jepsen, L. H.; Schouwink, P.; Černý, R.; Ravnsbæk, D. B.; Filinchuk, Y.; Dornheim, M.; Besenbacher, F.; Jensen, T. R. Metal borohydrides and derivatives – synthesis, structure and properties. *Chem. Soc. Rev.* **2017**, *46*, 1565–1634.

(41) Ley, M. B.; Jørgensen, M.; Černý, R.; Filinchuk, Y.; Jensen, T. R. From M(BH4)3 (M = La, Ce) Borohydride Frameworks to Controllable Synthesis of Porous Hydrides and Ion Conductors. *Inorg. Chem.* **2016**, *55*, 9748–9756.

(42) Senoh, H.; Kiyobayashi, T.; Kuriyama, N.; Tatsumi, K.; Yasuda, K. Electrochemical reaction of lithium alanate dissolved in diethyl ether and tetrahydrofuran. *J. Power Sources* **200**7, *164*, 94–99.

(43) Ley, M. B.; Paskevicius, M.; Schouwink, P.; Richter, B.; Sheppard, D. A.; Buckley, C. E.; Jensen, T. R. Novel solvates M(BH4)3S(CH3)2 and properties of halide-free M(BH4)3 (M = Y or Gd). *Dalton Trans.* **2014**, *43*, 13333–13342.

(44) Richter, B.; Grinderslev, J. B.; Møller, K. T.; Paskevicius, M.; Jensen, T. R. From Metal Hydrides to Metal Borohydrides. *Inorg. Chem.* **2018**, *57*, 10768–10780.

(45) Kottam, P. K. R.; Kalkan, D.; Wohlfahrt-Mehrens, M.; Marinaro, M. Influence of Li-Salt Concentration on Redox Potential of Lithium Metal and Electrochemistry of Ferrocene in DMSO-Based Electrolytes. *J. Electrochem. Soc.* **2019**, *166*, A1574.

(46) Cengiz, E. C.; Rizell, J.; Sadd, M.; Matic, A.; Mozhzhukhina, N. Review—Reference Electrodes in Li-Ion and Next Generation Batteries: Correct Potential Assessment, Applications and Practices. *J. Electrochem. Soc.* **2021**, *168*, 120539.

(47) Brandreth, D. A.; Molstad, M. C. Solubilities of LiBH4 and LiH in Diethyl Ether. *J. Chem. Eng. Data* **1962**, *7*, 449–450.

(48) Marks, T. J.; Kolb, J. R. Covalent transition metal, lanthanide, and actinide tetrahydroborate complexes. *Chem. Rev.* 1977, 77, 263–293.
(49) Wieser, H.; Laidlaw, W. G.; Krueger, P. J.; Fuhrer, H. Vibrational

spectra and a valence force field for conformers of diethyl ether and deuterated analogues. *Spectrochim. Acta, Part A: Mol. Spectrosc.* **1968**, 24, 1055–1089.

(50) Shirk, A. E.; Shriver, D. F. Solvent and cation dependence of the tetrahydroborate, BH4-, Raman spectrum. *J. Am. Chem. Soc.* **1973**, *95*, 5901–5904.

(51) Watkins, T.; Kumar, A.; Buttry, D. A. Designer Ionic Liquids for Reversible Electrochemical Deposition/Dissolution of Magnesium. *J. Am. Chem. Soc.* **2016**, *138*, 641–650.

(52) Ta, K.; Zhang, R.; Shin, M.; Rooney, R. T.; Neumann, E. K.; Gewirth, A. A. Understanding Ca Electrodeposition and Speciation Processes in Nonaqueous Electrolytes for Next-Generation Ca-Ion Batteries. *ACS Appl. Mater. Interfaces* **2019**, *11*, 21536–21542.

(53) Ley, M. B.; Boulineau, S.; Janot, R.; Filinchuk, Y.; Jensen, T. R. New Li Ion Conductors and Solid State Hydrogen Storage Materials: LiM(BH4)3Cl, M = La, Gd. J. Phys. Chem. C 2012, 116, 21267–21276.

(54) Attias, R.; Chae, M. S.; Dlugatch, B.; Oliel, M.; Goffer, Y.; Aurbach, D. The Role of Surface Adsorbed Cl- Complexes in

Rechargeable Magnesium Batteries. *ACS Catal.* **2020**, *10*, 7773–7784. (55) Joo, T. H.; Kim, K.; Kim, M. S. Surface-enhanced Raman study of

organic sulfides adsorbed on silver. J. Mol. Struct. **1987**, *162*, 191–200. (56) Noack, K.; Kiefer, J.; Leipertz, A. Concentration-Dependent Hydrogen-Bonding Effects on the Dimethyl Sulfoxide Vibrational Structure in the Presence of Water, Methanol, and Ethanol. ChemPhysChem **2010**, *11*, 630–637.

(57) Wright, A. M.; Howard, A. A.; Howard, J. C.; Tschumper, G. S.; Hammer, N. I. Charge Transfer and Blue Shifting of Vibrational Frequencies in a Hydrogen Bond Acceptor. *J. Phys. Chem. A* **2013**, *117*, 5435–5446.

(58) Schweizer, K. S.; Chandler, D. Vibrational dephasing and frequency shifts of polyatomic molecules in solution. *J. Chem. Phys.* **1982**, *76*, 2296–2314.

(59) Bartenbach, D.; Wenzel, O.; Popescu, R.; Faden, L.-P.; Reiß, A.; Kaiser, M.; Zimina, A.; Grunwaldt, J.-D.; Gerthsen, D.; Feldmann, C. Liquid-Phase Synthesis of Highly Reactive Rare-Earth Metal Nanoparticles. *Angew. Chem., Int. Ed.* **2021**, *60*, 17373–17377.

(60) Moulder, J. F.; Chastain, J., Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data; Physical Electronics Division, Perkin-Elmer Corporation: 1992.