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ABSTRACT

Borohydride-based electrolytes have recently emerged as promising media for the electrodeposition of electropositive metals, including rare earth (RE) elements. While the presence of supporting alkali metal cations and RE counter anions provides essential electrochemical conductivity for achieving fast metal electrodeposition, the interactions between the host ligand and solvated neodymium (Nd) complexes remain unclear. This study provides insights into the coordination structure of a concentrated and directly solvated Nd salt in lithium borohydridesupported electrolyte. Our spectroscopic results indicate that the RE coordination environment is significantly influenced by the solvation mechanism, which can vary between metathesis and complexation pathways, primarily dictated by stoichiometric factors. Under dilute conditions, nearly complete metathesis of anions leads to a high coordination number for the host ligand (borohydride), consistent with previously reported solvated Nd speciation in chlorine-free electrolytes. In contrast, concentrated dissolution of the Nd salt in the supported electrolyte is dominated by a complexation pathway featuring a Li ion-paired complex with a low coordination number of the host ligand. Density Functional Theory (DFT) calculations indicated that the observed blue shift in the borohydride vibration was the result of an increase in electron density drawn into the terminal B-H interbond region from the hydride as coordination changed from Li to Nd. In conjunction with DFT results, vibrational analyses allowed correlation of the experimental shifts associated with changes in Nd ligation and coordination sphere, further consolidating the prevalence of high chloride-coordinated species under concentrated conditions. The outcomes of this work illuminate the distinctive and heterogeneous coordination structures that the electroactive RE species can adopt at high concentrations in lithium borohydridesupported electrolytes, as a key step to comprehend the reported metal electrodeposition performance in these media.

INTRODUCTION

Owing to their exceptional magnetic properties, rare earth (RE) elements are indispensable in modern technologies, particularly in electronic devices like permanent magnets and batteries [^{1–3}]. Ensuring a secure supply chain of these critical materials has become imperative for sustainable economies. The escalating demand for these elements has spurred research into alternative technologies aimed at replacing the environmentally unfriendly and energy-inefficient molten salt process [^{2,4,5}]. Therefore, electrochemical production of RE metals under ambient conditions has emerged as a burgeoning research area. Various room temperature electrolytes have been explored, including conventional ionic liquids (ILs), molecular solvents, and ligand-based electrolytes [^{6–9}]. Despite substantial research efforts, achieving high efficiency and product quality in these room temperature electrolyte systems remains a significant challenge.

Unveiling the nature of RE coordination is key to designing efficient electrolytes, operating under ambient conditions. Given their unique properties, including intrinsic conductivity and large electrochemical window, the use of ionic liquids as electrolyte media has dominated the room temperature RE electrodeposition studies [^{10–14}]. The coordination of REs in ILs has been extensively explored using conventional spectroscopic methods [^{15–23}]. In these studies, the dissolution of RE salts in ILs occurs primarily through anions binding to the metal center, resulting in a coordination number typically ranging from 8 to 10. Spectroscopic investigations in triflate-based ILs have revealed that RE metals often coordinate through oxygen binding sites, forming

either bidentate or tridentate complexes. The presence of water and the hygroscopic nature of RE salts have been found to alter RE speciation and the efficiency of electrodeposition process in ILs [^{22,24,25}]. Consequently, efforts have focused on designing electrolyte systems that are devoid of water to optimize the electrochemical production of RE metals under ambient conditions.

Borohydride-based electrolytes have recently emerged as promising media for the electrodeposition of electropositive metals such as Ca, Mg, Nd, and Dy [26,27]. The anhydrous nature of borohydride electrolytes helps prevent the hygroscopic nature of RE salts, which can otherwise alter the electrodeposition process when exposed to water. Moreover, borohydride electrolytes offer a fluorine-free environment, preventing the formation of a passivation layer at the electrochemical interface [$^{27-31}$]. While the electrodeposition of Ca and Mg metals has demonstrated efficient and reversible processes in these electrolytes, Nd and Dy metal electrodeposition in similar borohydride electrolytes has been observed to result in reacted RE metal, with significant impurities in the final products.

Dissolution of RE (e.g. Nd) in borohydride-based electrolyte occurs by reacting Nd salts (i.e. chloride or triflate) with alkali and/or alkali earth borohydride electrolytes [^{27–29}]. This reaction is typically understood as involving the exchange of the counter anions of the Nd³⁺ metal center with the host borohydride ligand through metathesis. Stoichiometric metathesis, facilitated by ball milling, achieves complete exchange of Cl⁻ with BH4⁻ anions and results in complete precipitation of LiCl [²⁹]. However, such solutions of highly pure Nd(BH4)₃ were reportedly non-conductive and inadequate as electrolytes for metal electrodeposition, as evidenced by high impedance and no observed voltammetric current. Therefore, effective electrolytes require supporting electrolytes such as Li/Na/ammonium salts to achieve working conductivity. Preparation of these supported electrolytes could be achieved either via indirect dissolution of pre-isolated RE-borohydride-

solvent complex or direct reaction of the RE salt precursors to the borohydride-based electrolyte, as a facile synthetic pathway [^{27–29}]. Despite the advantages of these supported electrolytes, deposits obtained in these systems often exhibit reacted materials with high impurity content. Moreover, the exact reduction mechanism in these electrolytes, whether through direct or mediated electron transfer at the RE metal center, remains unclear. For instance, voltammetric analysis of dissolved Nd salt in Li-supported electrolyte reveals reversible Li metal deposition/stripping, yet with no distinct faradaic current attributable to Nd reduction [²⁹].

An essential step in addressing these mechanistic and structural questions is to elucidate the nature of the solvation environment of the electroactive RE speciation in borohydride electrolytes. While borohydride is commonly believed to coordinate with the RE metal center at the boron site, it can also adopt bidentate or tridentate binding modes involving bridging protons [^{32–34}]. The coordination of borohydride in inorganic complexes has been extensively documented, primarily focusing on solid and isolated complexes in existing literature.

Given the limited reports in these systems, the speciation of solvated RE complexes in the borohydride-supported electrolytes, as working electroplating systems, and associated coordination sphere have not been thoroughly characterized. While the presence of supporting alkali or alkaline earth metals and Nd salt counter anion enhances electrochemical conductivity (higher ionic strength), their interactions with solvated Nd complexes remains ambiguous. These coordination interplays become important in the directly dissolved and Nd concentrated electrolyte, as an easy prepared and desired system to achieve efficient and robust metal electrodeposition process. From an electrostatic standpoint, association of solvated Li⁺ cation with an anionic Nd complex via ion-paring interactions may involve the co-solvation of the counter anion (Cl⁻). Within a heterogenous and competing ligand environment in lithium borohydride-

supported electrolyte, stochiometric factors are expected to dictate the dominant reaction pathway for Nd dissolution and the associated coordination sphere. Hence, this work aims to provide an insight on the coordination structure of directly solvated Nd complexes at high concentrations in the lithium borohydride-supported electrolyte. While this work focuses on Nd element, considering recent reports in borohydride electrolyte systems, the outcomes of this study could be extended to other comparable electropositive RE elements, such as Dy. Electronic and vibrational analyses of solvated Nd complexes in the studied electrolyte conditions were substantiated through density functional theory (DFT) calculations. The outcomes of this work illuminate the distinctive coordination structures that Nd can adopt within concentrated and lithium borohydride-supported electrolytes, as a key step to comprehend the observed electrodeposition performance in these media.

EXPERIMENTAL

Chemicals: Neodymium chloride (NdCl₃, anhydrous powder, \geq 99.99% trace metals basis), lithium borohydride (LiBH₄, 2M in THF) and tetrahydrofuran (THF, anhydrous, inhibitor-free, \geq 99.9%) were purchased and used without further purification. Preparation of Nd-loaded electrolyte solutions was performed, under inert glovebox (UHP Argon) environment, via dissolution of varying amount of anhydrous NdCl₃ in typically 0.4M LiBH₄ in THF, which were allowed to stir overnight. Following dissolution, the solutions were filtered to obtain clear purple color with negligible precipitation.

Characterization: Visible-near-infrared (Vis-NIR) spectra of solutions were taken in a quartz cuvette that had been filled and sealed inside argon-filled glovebox. Vis-NIR spectra were

collected on a Shimadzu UV 3600 Plus, using 0.5 nm resolution. Nd quantification in the deposited samples was measured using an iCAP Q inductively coupled plasma mass spectrometer (ICP-MS) from Thermo Scientific. Infrared spectra were carried using an argon sealed attenuated total reflection (ATR) cell. Infrared (IR) measurements were collected using a dry air-purged Bruker Vertex 70 FTIR spectrometer, coupled to a liquid nitrogen-cooled HgCdTe (MCT) detector. Spectra were collected using a 2 mm aperture, 40 kHz scanning velocity and 4 cm⁻¹ resolution. Spectral deconvolution of infrared spectra was performed using GRAMS (Thermo Scientific) software.

Computational: DFT calculations were performed using the Gaussian Rev C.02 suite of software using the B3LYP level of theory $[^{35-37}]$. Empirical dispersion was employed using the D3 version of Grimme's dispersion correction with Becke-Johnson damping $[^{38,39}]$. Per convention, this combination will be referred to as B3LYP-D3(BJ). DFT calculations are used to assign vibrational bands, to help understand how changes in band intensities connect to changes in borohydride coordination, and to examine energetic trends in Nd coordination. The B3LYP functional, with the addition of D3(BJ), has been shown to balances reasonable accuracy and computational cost for a wide variety of systems, including ones involving non-covalent interactions and those containing Nd [^{23,40}]. All calculations utilize the Def2-TZVPP basis set retrieved from the Basis Set Exchange, which for Nd includes a relativistic effective core potential and is generally recommended $[^{41-44}]$. All calculations were conducted using a pruned (99,590) grid (Gaussian keyword int=ultrafine). The influence of the THF solvent environment was modeled using the conductor-like polarizable continuum model (CPCM). Counterpoise corrections were not employed as they cannot be used in conjunction with self-consistent reaction field (SCRF) solvent models. However, calculations utilizing counterpoise correction

and no SCRF model showed estimated Basis Set Superposition Errors of less than 1.5 kJ/mol, which is lower than expected method errors

The structures of all studied systems were optimized to stationary points using Gaussian tight criteria. Frequency calculations were conducted to verify optimized structures were at stationary points and for comparison to experimental vibrational spectra. The stability of the calculated wavefunctions of the optimized geometries were verified using the Gaussian stable keyword. Calculated frequencies were scaled by 0.963, based on the pre-computed scaling factors available in the National Institute of Standards and Technology (NIST) Computational Chemistry Comparison and Benchmark DataBase (CCCBDB) for B3LYP with an ultrafine grid and the TZVP basis set. While the Def2-TZVPP basis set is different from the TZVP basis set, they are similar enough to justify using the same scaling factor.

Electron density difference (EDD) maps were calculated from single point energy calculated wavefunctions exported as wfx files (Gaussian keyword output=wfx). Single point energy calculations for the parent structure (LiNdCl₃BH₄, for example) and the fragments ([LiNdCl₃]⁺ and [BH₄]⁻, for example) were conducted using the Gaussian nosymm keyword, which suppresses the conversion of the molecular coordinates into new internal coordinates. This ensures that the coordinates of all the atoms in the two fragments are the same as they are in the parent structure. The two fragment electron densities were subtracted from the parent electron density and plotted using Multiwfn [⁴⁵]. Counterpoise corrections were not employed as they cannot be used in conjunction with self-consistent reaction field (SCRF) solvent models. As the purpose of the calculated EDD maps was to explore the origin of the shift in BH₄ infrared frequencies rather than for making quantitative calculations, and counterpoise corrections for

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calculations with no SCRF models were small, the lack of counterpoise corrections for the EDD calculation is not concerning.

RESULTS AND DISCUSSION

Neodymium dissolution

The investigation into Nd solvation in a lithium borohydride electrolyte began by examining electronic spectra at various concentrations. Direct Nd dissolution was achieved by reacting NdCl₃ with a LiBH₄-based solution in THF. As with previously reported, solvated Nd complexes in our studied electrolytes featured purple colored solutions [$^{27-29}$]. Quantification of Nd concentrations in these solutions was conducted via elemental analysis with ICP-MS, results of which are presented in Table S1. The solubility of NdCl₃ in the 0.4M LiBH₄/THF solutions exceeds 100mM of Nd, which is a sharp contrast to the previously reported calcium borohydride system, where Nd concentrations were found to be <80 mM in 0.45M Ca(BH₄)₂/THF solutions [28]. This disparity is likely due to differences in valence and borohydride coordination between calcium and lithium metals.

Visible-Near Infrared (Vis-NIR) spectra were collected at different Nd concentrations, as shown in Figure S1. Figure 1 illustrates the Nd electronic transitions in a selected visible range of concentration-normalized spectra at the wavelength of maximum absorbance ($\lambda_{max} = 584$ nm), ascribed to the Nd 4*f* shell hypersensitive (⁴I_{9/2} to ⁴G_{7/2}) transition [^{27,33,46}]. NIR absorbance demonstrates a linear relationship with Nd concentrations, further supporting complete Nd salt dissolution in the studied electrolyte conditions. More important changes could be observed in the overlayed normalized spectra, obtained at different concentrations (Figure 1). Interestingly, increasing Nd concentrations resulted in heightened shoulder peaks at 578 nm and broadening around 600 nm, accompanied by slight but measurable red shifts from 585 nm to 586 nm across all NIR peaks. Notably, at equimolar conditions, a more pronounced 2 nm red shift was observed at higher (from 807 to 809 nm) wavelengths (Figure S1). While spectra obtained at higher (80-100mM) Nd concentrations look similar (but not identical), they show substantial difference from the low Nd concentration spectrum. The molarity ratio, $[Li^+]/[Nd^{3+}]$ or $[BH4^-]/[Nd^{3+}]$, in this later spectrum is about one order of magnitude higher (ratio~20), as compared to very concentrated solutions (ratio< 5).



Figure 1. Recorded visible spectra in the hypersensitive peak range of various Nd-loaded solutions in 400 mM LiBH₄ in THF, at different Nd concentrations. The inset highlights the slight but noticeable red shift in the hypersensitive peak through the different listed Nd concentrations

The changes observed in the electronic spectra indicate a shifting Nd speciation dependent on Nd concentration or stoichiometric ratio. Inspection of the normalized spectra revealed at least two distinct Nd species depending on the Nd concentration. Such evolution of speciation prompts a crucial question into the pathways through which NdCl₃ salt interacts with the LiBH₄ electrolyte.

Given the limited solubility of polar NdCl₃ in the nonpolar solvent THF (with a dielectric constant of approximately 7), Nd³⁺ solvation primarily involves coordination with the BH₄⁻ anion. The coordination of BH₄⁻ with the Nd metal center is indicated by a shoulder peak at approximately 591 nm [^{27,33}]. However, borohydride ligation in solution may proceed via distinct reaction pathways, resulting in various distinct Nd speciation.

Dissolution of neodymium chloride salts in organic solvents has been generally described to proceed via metathesis exchange of chloride anions with host ligand, borohydride anions [^{27–29}]. This reaction is expected to be near complete under high excess of borohydride anion (high stoichiometric ratio). This leads to a complete solvation of Nd³⁺ with borohydride ligand and loss of Cl⁻ counter anions from the metal coordination sphere (Reaction A). Dissolution of insoluble NdCl₃ is promoted by the precipitation of the more stable LiCl co-product in THF. Such stoichiometric exchange could be obtained with slow solid-state synthesis via ball milling reaction, leading to a near Li-free Nd-borohydride complex [²⁹]. However, under solution conditions, a Li⁺ ion-paired Nd complex can be envisioned (Reaction B), due to the high coordination number (8 to 10) that Nd³⁺ metal cation typically allows [⁴⁷]. Thus, both A and B reaction pathways lead to borohydride-only coordinated Nd complexes.

 $NdCl_{3}(s) + 3LiBH_{4} \rightarrow Nd(BH_{4})_{3} + 3LiCl(s)$ (Reaction A) $NdCl_{3}(s) + 4LiBH_{4} \rightarrow Li-Nd(BH_{4})_{4} + 3LiCl(s)$ (Reaction B)

By contrast, under small stoichiometric ratio where the borohydride becomes a limiting reagent, the concentrated dissolution of NdCl₃ is expected to proceed through an addition (complexation) reaction. In this later pathway, both counter anion and host ligand are retained in the coordination sphere of the solvated Nd^{3+} metal cation, according to Reaction C. Given its high coordination number, the formed Nd species is also a Li⁺ ion-paired complex [⁴⁷].

$$NdCl_3 + LiBH_4 \rightarrow Li-NdCl_3(BH_4)$$
 (Reaction C)

Overall, excluding the solvent from the coordination representation, the possible Nd speciation in upon direct Nd salt dissolution in the supported electrolyte are metathesis products (Nd(BH4)3, Li- $[Nd(BH_4)_4)]$ addition product Li-[NdCl₃(BH₄)], with possible intermediate and metathesis/addition species (Li-[NdCl_x(BH4)_y]ⁿ⁻, where x+y=n-3). Interestingly, elemental analysis of the prepared solutions reveals that Li content stays constant throughout all added NdCl₃ concentrations. Given the insolubility of LiCl in the nonpolar THF, the solvated Nd complex must therefore include Li⁺, likely as ion-paired product. Consequently, Equation B is likely more descriptive of Nd dissolution under metathesis reaction pathway. This excludes the presence of the stochiometric product Nd(BH4)3, in favor of the ion-paired Li-[Nd(BH4)4] complex in the electrolyte. Given the insolubility of the NdCl₃ salt, free (THF-solvated) Nd³⁺ or NdCl₃ species are not expected to exist in the studied electrolyte.

Vibrational Analysis

The electronic spectra indicated changes in Nd speciation depending on stoichiometric conditions. However, the coordination environment of the solvated metal complex appears to encompass various possible coordination compositions. To gain deeper insights into the nature of the solvated Nd complex, vibrational analyses were conducted. Infrared spectra were recorded while varying the Nd concentration in the LiBH₄-based electrolyte, as depicted in Figure 2. It is noteworthy that this analysis takes advantage of the intense and distinctive vibrational modes of borohydride above 2000 cm⁻¹, bypassing the need to interpret the complex spectral changes in the fingerprint region [⁴⁸]. In the spectrum obtained from the Nd-free solution, two major intense and broad bands at 2220 and 2325 cm⁻¹ are observed, corresponding to the stretching modes of B-H bonds in the LiBH₄ electrolyte in THF [⁴⁹].

The introduction of NdCl₃ salt results in the appearance of a distinctive new band at higher energies (2420 cm⁻¹). Similar bands have been previously reported for isolated Nd-borohydride complexes [^{50,51}]. This newly emerged band increases in intensity with higher Nd concentrations in the solutions under study. This vibrational signature is attributed to the formation of solvated Nd complexes in the Li-based electrolyte. Importantly, the intensity increase of this new band correlates with a significant decrease in the initial broad band observed at 2330 cm⁻¹ in the Nd-free solution. These vibrational changes suggest the substitution of borohydride anions from Li coordination, the coordination number of borohydride to Nd metal can be estimated using a previously reported approach [^{47,52}].



Figure 2. (Left) Recorded infrared spectra of varying Nd-loaded solutions in 400 mM LiBH₄ in THF, at different Nd concentrations. (Right) Infrared-calculated Nd-borohydride coordination number as obtained from the y-intercept of the linear regression of the ratio of LiBH4 peak intensity to the concentration of

Nd (*y*-axis) versus the ratio of the total concentration of borohydride species to the concentration of Nd (*x*-axis).

The solvation number (n) of the Nd complex with borohydride can be determined from Equation 2, which incorporates the concentration (M_Li) and intensity (I_Li) of the 2330 cm⁻¹ band, as well as the absorption coefficient (J_Li) of Li-coordinated borohydride. Additionally, it includes the Nd concentration (M_Nd) and intensity (I_Nd) of the corresponding band for Nd-coordinated borohydride. This calculation considers the total molarity of borohydride anions in the electrolyte.

As shown in Figure 2, the plot of of I_Li/M_Nd as function of M_total/M_Nd yields a straight line. From this linear relationship, the solvation number (n) can be determined from the intercept and slope of the fitted line. Based on this analysis, a borohydride coordination number between 1 and 2 is obtained for the solvated Nd complex under studied electrolyte conditions. Such a low borohydride coordination number suggests a mixed coordination environment around the Nd metal center. In addition to borohydride coordination, chloride anions and solvent molecules are expected to complete the coordination sphere of the solvated Nd species. This result is consistent with potential addition mechanism involving complexation of NdCl₃ salt with the host electrolyte. These results support the earlier proposed variations in reaction pathways. However, it should be noted that due to significant overlap in IR bands between Li-coordinated and Nd-borohydride complexes, the calculated IR coordination number remains qualitative in nature at this stage. Due to the significant variability observed in the IR bands, Raman spectroscopy was employed to further evaluate the borohydride coordination number in the solvated Nd complex in the supported electrolyte under study. Figure S2 presents acquired Raman spectra as a function of the introduced Nd concentration. As anticipated, the Raman spectra exhibit distinct and metal-specific borohydride vibrations within the 2200-2500 cm⁻¹ range. The spectrum obtained from the Nd-free solution displays a prominent band at 2304 cm⁻¹, attributed to the Li-coordinated borohydride anion. Upon the introduction of Nd into the Li-based electrolyte, two new bands emerge at 2250 cm⁻¹ and 2430 cm⁻¹, corresponding to Nd-coordinated borohydride anions [²⁹]. Consistent with the observed changes in the infrared spectra, increasing Nd concentration results in a significant decrease in the intensity of the 2300 cm⁻¹ vibration, accompanied by a simultaneous increase in the intensity of the 2250 cm⁻¹ band in the Raman spectra. These Raman spectroscopic changes support the exchange of borohydride coordination from Li to the Nd metal center. At high (above 120mM) Nd concentrations, it appears that coordination by Li is completely replaced by Nd-borohydride ligation.



Figure 3. (Left) Fitted Raman spectra of varying Nd-loaded solutions in 400 mM LiBH₄ in THF, at different Nd concentrations. (Right) Raman-calculated Nd-borohydride coordination numbers calculated similarly to those in Figure 2. Two coordination environments are observed, with high and low Li/Nd molar ratios

Taking advantage of the inherently distinct Raman peaks, the coordination number of borohydride to the Nd metal center was assessed using the same method (Equations 1 and 2). Figure 3 presents the results obtained from Raman intensities at various concentrations. Consistent with the infrared analysis, an overall coordination number of 2 was deduced from the linear regression. However, a closer examination of the observed linear correlations reveals that the slope appears to be divided into two concentration regions. At lower Nd concentrations (higher slope), a coordination number of 3 seems to be more descriptive of the plotted data. Conversely, in the high Nd concentration region, a significantly lower coordination number of approximately 1.4 was derived. The Raman analysis suggests a higher exchange of borohydride anions at lower Nd concentrations (higher stoichiometric ratio), indicating increased interaction with the Nd salt. Conversely, a lower number of coordinated borohydrides is observed at higher Nd concentrations (smaller stoichiometric ratio). Overall, the vibrational analyses indicate a mixed coordination Nd complex, suggesting incorporation of chloride and borohydride anions within the solvated Nd coordination sphere.

DFT Calculations

DFT calculations were employed to gain deeper insights into the coordination sphere of solvated Nd species in the studied supported electrolyte. These computational efforts encompassed various analyses, including vibrational analysis, charge density analysis, and free energies of reactions. Multiple structures with different coordination compositions were optimized at the B3LYP-D3(BJ) level of theory. Reaction free energies were calculated to investigate various pathways of NdCl₃ with LiBH₄ (Table S2).



Figure 4. DFT-calculated free energies (KJ/mol) for different Nd solvation reactions in the supported Liborohydride electrolyte. Calculations were conducted at the B3LYP-D3(BJ) level of theory with the Def2-TZVPP basis set for all atoms.

As displayed in Figure 4, borohydride binding to the metal center is through three bridging hydride atoms, forming a tridentate coordination pocket. From an energetic standpoint, complete displacement of chloride by borohydride appears to be thermodynamically uphill, which could be consistent with the difficult reaction under experimental conditions (necessitating overnight stirring). Moreover, a lower coordination number of borohydride appears to be thermodynamically more favorable. This is consistent with Hard Soft Acid Base theory, where the BH4⁻, as a larger, more polarizable species, would be considered a softer base than Cl⁻, and thus would not interact as strongly with the very hard Nd³⁺ acid. The formation of the trichloride-coordinated Nd complex emerges as the most favorable reaction pathway based on these calculations.

A key focus of the DFT analysis was to understand the nature of the newly observed IR band upon the introduction of Nd salt. Calculated IR spectra are compiled in Figure S3. The analysis of borohydride vibrational modes in the LiBH₄ electrolyte in THF revealed that the stretching modes of borohydride bridge and terminal groups were computed around 2210 and 2382cm⁻¹, respectively. These vibrational modes are assigned to the experimental IR bands at 2220 and 2325cm⁻¹, respectively. Comparable energies to the experimental bands have been reported for the bridge and terminal BH4⁻ stretching in isolated borohydride-based complexes [⁴⁹]. As discussed earlier, Li⁺ ion-paired of highly (tetra or more) coordinated Nd species are likely more prevalent than neutral (tri-coordinated) complexes in the (solution) electrolyte conditions. Therefore, Li-[Nd(BH4)4] and Li-[NdCl₃BH4] complexes, excluding the solvent molecules, were mostly considered for further vibrational analysis. Based on calculated frequencies, the borohydride ligation to the Nd metal center generally shows a blue shift of the terminal stretching to higher energies compared to LiBH4. This finding is consistent with the observed new broad band emerging at 2415-2435 cm⁻¹.



Figure 5: EDD map calculated at the B3LYP level of theory. The presence of $[LiNdCl_3]^+$ pulls electron density from the terminal hydride into the $B-H_{terminal}$ bond region, resulting in a blue shift of the $B-H_{terminal}$ stretch IR frequency compared to free $[BH_4]^-$. Coordination with Nd pulls more electron density into the $B-H_{termina}$ bond region than coordination with lithium, resulting in the experimentally observed blue shift in the IR spectra.

The shifts in the terminal borohydride IR frequencies upon changes in coordination can be understood by examination of the calculated electron density. Figure 5 shows an EDD map for Li-[NdCl₃BH₄] calculated at the B3LYP-D3(BJ) level of theory, which represents the change in calculated electron density as [Li-NdCl₃]⁺ and [BH₄]⁻ come together to form Li-[NdCl₃BH₄]. Coordination of a center of positive charge with the bridge hydrides in [BH4]⁻ pulls electron density into B-H_{terminal} interbond region, strengthening the bond and thus shifting the IR stretching frequency to higher energies. Electron density is also pulled from the bridging hydrides but not into the B—H_{bridging} bond region, rather into the pocket formed by the three bridging hydrides and the boron. The electron density in the B—H_{bridging} bonds is minimally perturbed by coordination, so IR frequencies involving those bonds do not shift much upon coordination. Different coordinating species pull different amounts of electron density into the B-Hterminal interbond region, and thus result in different B—Hterminal stretching frequencies. For example, coordination with [Li-NdCl₃]⁺ pulls more electron density into the B—H_{terminal} interbond region than coordination with [Li]⁺, resulting in a B—H_{terminal} stretching frequency for LiNdCl₃BH₄ that is blue-shifted compared to that of LiBH₄.

More importantly, the displacement of BH4⁻ with Cl⁻ anions in the Nd coordination sphere slightly shifts the terminal stretching to lower energies (Figure S3). The chloride-coordinated Nd metal center appears to pull less electron density, resulting in weaker B—H_{terminal} bond, as compared to the fully borohydride-coordinated Nd complex. Upon closer inspection of the broad experimental IR band, it appears that the emerging peak can be resolved into two overlapping bands, which deconvolute into bands centered at 2436 and 2416 cm⁻¹ (Figure 6). This is consistent with the predicted red shift in in the B—H_{terminal} vibration. It is noteworthy that the difference between DFT-calculated shift (~2 to 6 cm⁻¹ lower) and the experimental shift (~20 cm⁻¹ lower), due to Nd

chlorination, likely reflects more intricate intermolecular interactions with the solvent and Li-ion pairing. Interestingly, overlaying the deconvoluted bands obtained at two Nd concentrations, 120 mM and 350 mM, reveals a dominant evolution of a red-shifted band (2416cm⁻¹) at higher Nd concentrations, relative to 2436 cm⁻¹. These findings support the prevalence of chlorinated Nd species at higher concentrations, as suggested by the aforementioned analyses.



Figure 6. Experimentally obtained Nd-borohydride infrared bands at two different Nd concentrations in the supported electrolyte (400 mM LiBH4 in THF). The fitted data (blue) has been deconvoluted into two smaller bands that are due to low Nd-chloride and high Nd-chloride coordination environments

Chloride coordination is further substantiated through examination of the low energy region of the experimental Raman spectrum at high Nd concentration, which revealed a prominent vibration at 250 cm⁻¹ (Figure S4). This observed band aligns with DFT calculations for the chlorinated Nd complex, which predicted an intense symmetric Nd-Cl stretching vibration at 250 cm⁻¹. Furthermore, a high (>1M) chloride concentration was qualitatively confirmed through elemental analysis (ICP) in the Nd-rich solution. Considering the insolubility of NdCl³ and LiCl in nonpolar

THF, the presence of chloride in the electrolyte is consistent with its coordination to the solvated Nd metal complex.

CONLCUSION

In this work, we investigated the coordination structure of a directly solvated and concentrated Nd salt in lithium borohydride-supported electrolyte. Our spectroscopic analyses indicated that the metal coordination environment is significantly influenced by the solution reaction mechanism, which can vary between metathesis and addition pathways. The nature of dominant reaction pathway depends on stoichiometric factors. When the Nd concentration is low, host ligands effectively displace counter anions through complete metathesis exchange, resulting in a high coordination number with borohydride anions. Conversely, concentrated Nd dissolution is primarily driven through an addition reaction, maintaining the presence of counter anions within the Nd coordination sphere but with a lower coordination number of the host ligand. Vibrational analyses revealed specific Nd-borohydride coordination signatures, outside the fingerprint region. DFT analyses further elucidated changes in electron density around terminal B-H bonds and associated vibrational shifts upon Nd introduction. These shifts and calculated borohydride coordination numbers were consistent with the prevalence of chloride-coordinated species at higher Nd concentrations

In conclusion, this study underscores the sensitivity of RE coordination environment to electrolyte conditions. Complexation reactions allow highly conductive and concentrated electrolytes, which are essential to reach fast metal electroposition rates. However, the heterogeneous coordination environment within the Nd solvation shell, involving counter anions and host ligands, may

significantly influence the efficiency of the electrodeposition process in these electrolytes. For instance, due to the high electropositivity of RE metals, alteration to the metal solvation structure may lead to additional overpotentials, bringing the reduction thermodynamics closer to the edge of the electrochemical window of the electrolyte (comprising solvent and ions). Under conditions of non-equilibrium or limited mass transport at the very negatively polarized electrochemical interface, side reduction processes involving the altered electroactive RE speciation might induce electrolyte reactivity and introduce metal impurities.

ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge.

Additional figures and tables for visible, infrared, DFT calculations, and elemental analyses data (Word Document).

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TOC Graphic

