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Enhanced Dissolution of Metal Oxides in Hydroxylated Solvents – Towards Application in Lithium-Ion Battery Leaching


The recovery of critical metals from spent lithium-ion batteries (LIBs) is rapidly growing. Current methods are energy-intensive and hazardous, while alternative solvent-based strategies require more studies on their ‘green’ character, metal dissolution mechanism and industrial applicability. Herein, we bridged this gap by studying the effect of dilute HCl solutions in hydroxylated solvents to dissolve Co, Ni and Mn oxides. Ethylene glycol emerged consistently as the most effective solvent, dissolving up to four times more Co and Ni oxides than using aqueous acidic media, attributed to improved chlorocomplex formation and solvent effects. These effects had a significant contribution compared to acid type and concentration. The highest Co dissolution (0.27 M) was achieved in 0.5 M HCl in 25% (v/v) glycerol in water, using less acid and a significant amount of water compared to other solvent systems, as well as mild temperatures (40°C). This solvent was applied to dissolve battery cathode material, achieving 100% dissolution of Co and Mn and 94% dissolution of Ni, following what was concluded to be a mixed mechanism. These results offer a simple alternative to current leaching processes, reducing acid consumption, enhancing atomic efficiency, and paving the way for optimized industrial hydrometallurgical processes leaning to ‘greener’ strategies.

Introduction

The progress towards carbon neutrality depends on the development of advanced technologies that will rely on energy storage systems. The demand for these, particularly lithium-ion batteries (LIBs), is projected to double current values in a great part due to the ‘boom’ in electric vehicles.[1] Consequently, the demand for the raw materials used in LIB manufacturing is rapidly increasing, particularly for Li, Co and Ni. Unfortunately the exploitation of these materials is not without its problems, namely geopolitical, environmental and social.[2] While novel LIB chemistries and designs are under development, including the reduction or exclusion of specific metals, the number of hazardous spent LIBs is rapidly increasing.[3,4] Thus, LIB recycling is crucial for both the mitigation of health and environmental concerns, but also as a secondary source of critical raw materials.[5]

Recycling of LIBs entails a mixed approach, combining mechanical pre-treatment of the waste with subsequent pyrometallurgical (thermal) and/or hydrometallurgical (chemical) treatment. Compared to pyrometallurgy, hydrometallurgy is touted as the environmentally friendlier alternative due to its lower energy requirements and gaseous emissions. It also allows the recovery of all metallic components from the black mass (the active electrode materials, after detachment from other components), including Li and Mn, thereby enabling the closed-loop regeneration of LIB cathodes.[6] Primary hydrometallurgical operations typically consist of a leaching stage followed by separation and purification stages, with the “green” character of the final process depending on overall toxicity and environmental impact of resulting waste effluents, often measured through life cycle assessments (LCAs). These LCAs, consistently identify the leaching and wastewater treatment stages as the biggest contribution to the environmental impact, making them targets for improving the “green” character of a system.[7] The 12 Principles of Green Chemistry by Anastas and Warner[8] can be used as a framework to develop “greener” processes. From them, one way to tackle this is through the reduction or removal of volumes of hazardous chemicals used, preventing waste. However, a simpler and comprehensive approach could be achieved through the design of an atomically efficient and/or selective leaching process as this will streamline downstream processing, using less chemicals/steps.[9] The use of non-aqueous media, solvometallurgy, has emerged as an alternative approach using milder solvents and more selective leaching conditions.[10] Amongst the various options, deep eutectic solvents (DESs) are an emerging class of mixtures characterized by a significant melting point depression below...
the ideal eutectic point, thereby increasing the accessibility of their liquid window. These mixtures of hydrogen bond donor (HBD) and acceptors (HBA), the latter often being a quaternary halide salt such as choline chloride (ChCl), were successfully applied towards the lixiviation and electrodeposition of a range of metals from various primary and secondary ores. The halide concentration in most DES, the potential inclusion of organic acids as HBD, and the low water concentration results in different leaching efficiency and selectivity towards chlorophilic metal cations compared to those obtained in aqueous media. Schiavi and colleagues used ChCl:ethylene glycol (ChCl:EG) to recover Li, Co, Ni and Mn from mixed LIB chemistries by two leaching steps at different temperatures. Up to 90% Co was recovered at 180°C, with only 10% Ni present in the extract, and the DES was reused after cobalt precipitation by aqueous Na₂CO₃ or oxalic acid addition, which is one of the largest advantages of using these solvents. Similarly, ChCl:oxalic acid was used by Thompson et al. to separate Co and Mn from Ni in a model black mass of a nickel manganese cobalt (NMC) LIB, at 80°C. Following leaching, Ni was selectively precipitated as Ni oxalate through the addition of water as a counter-solvent.

Despite their proven success, the underlying contributions of each DES component to the total leaching mechanism remains elusive as DES are often described as a poorly defined mix of interactions. Upon closer inspection, certain properties of DES appear in contradiction to their excellent solubilising capacity. For example, it is well known that the pKa of an organic acid can increase significantly as water is replaced by less polar solvents, affecting both the total proton concentration and its activity. The pKa values for nine organic acids were consistently about 0.5 units higher in 1:2 ChCl:EG than in water, which was explained by the greater relative basicity of the chloride anion compared to water. The weaker acid dissociation constant in DES is compensated by their high concentration as a DES phase former. This, however, negatively impacts the solvent toxicity, as is expected from typical organic acid concentrations of over 2.5 M, and defies the “green solvent” label associated with DES. A recent study on the leaching of LIBs in the ChCl:oxalic acid DES found that Co dissolution occurred through the oxidation of ChCl and the in-situ formation of HCl, casting doubt on the exact contribution of the organic acid. Additionally, by-products of ChCl degradation such as trimethylamine act as a basic pH buffer and could complicate metal recovery and DES reuse through the formation of metal-amine complexes. These stability issues are further compounded by the partial esterification of ChCl under common leaching temperatures, making the recycling of the DES phase over multiple cycles a non-trivial problem as well as affecting its toxicity. In fact, it was recently suggested that the ChCl:EG DES in the absence of an additional reducing agent will be less efficient for LIB leaching as metal oxide dissolution primarily occurs through the degradation of the DES components at high temperatures. This is not to say that DES do not have their merit, rather that simpler systems could be considered without compromising the leaching efficacy of DES and by better understanding their underlying contributions.

DES share some properties with molecular solvents including similar polarity, i.e., relative permittivity, as polyols since this property is mainly dependent on the HBD selection. For the leaching of metal oxides from LIBs, a decrease in the solvent polarity may result in increased ion-ion and ion-dipole correlations, which could favour both acid adsorption on the oxide surface and breaking of the metal-oxide bond during the leaching of metal oxides. Thus, the molecular solvents that often serve as HBD components in DES with stoichiometric addition of acid could fill the gap between a milder metal leaching system and one that is more easily applicable industrially. Hydroxylated compounds such as ethylene glycol have been used for metal extraction, either as additives to acidic aqueous solutions or as recovery media themselves. In both cases, significant enhancement in the metal dissolution was observed compared to the acidic aqueous solutions even at low fractions of solvent. Furthermore, the reducing capacity of hydroxylated compounds is relevant for leaching from LIBs, as metal oxides are often in mixed +2 to +4 oxidation states, depending on the metal cation, and require reduction for their efficient recovery.

In this work, four compounds with varying solvent permitivity – glycerol, ethylene glycol, 1,3-butandiol and 1-butanol – were used in conjunction with dilute HCl concentrations for the dissolution of Co, Ni and Mn oxides and extraction of these metals from NMC. The effect of the chemical composition of the solvent in the metal dissolution mechanism was investigated, considering the individual metals and when mixed in a complex matrix. HCl is a strong acid whilst also providing the chloride anion often found in DES, and other acids were compared to further understand the influence of the acid nature on metal dissolution. This work focuses on the contributions of all these components, especially those from the hydroxylated solvents that represent HBDs of DES, but without being within a DES system. The performance of mixtures of hydroxylated compounds and water, as an intermediate system with even milder environmental impact, was also assessed. Ultimately, these individual effects were rationalized to provide further insight into the metal dissolution mechanism, both of individual oxides as well as for the stoichiometric leaching of NMC.

Results and Discussion

Cobalt dissolution in hydroxylated solvents

To assess both the feasibility of simpler solvometallurgical approaches and to better understand the role of the individual components of a complex solvent system in metal dissolution, a range of hydroxylated solvents were selected for metal oxide (MO) dissolution using HCl as lixiviant (Figure 1a). The tested solvents – glycerol (Gly), ethylene glycol (EG), 1,3-butandiol (BdOH) and 1-butanol (BuOH) – were selected based on their reported use as HBD in DES or as aqueous additives for metal leaching. This solvent selection also allows to assess the effect of permittivity, the number of hydroxyl moieties and...
dentation, as these can influence metal complexation and consequently contribute to metal dissolution, especially in the presence of halides.\textsuperscript{[23]} Hydrochloric acid was used as the acid component of the metal dissolution media due to its dual action as a proton (acidity) and chloride (Cl\textsuperscript{−}) source, assuming full dissociation. Despite being a hazardous chemical by itself, concentrations were kept low as its purpose was to allow the study of these two contributions to metal dissolution, not accessible with other inorganic acids. These systems are not DES, but only mixtures of HCl and hydroxylated solvents. This fulfils an intermediate type of system: between using aqueous mineral acid solutions – in hydrometallurgy – and DES – an example of solvometallurgy.

Due to its economic relevance in waste LIBs, the dissolution of cobalt (II) oxide (CoO) and cobalt (III) oxide (Co\textsubscript{3}O\textsubscript{4}) in these solvents was investigated first, prior to extending the study to other oxides and NMC 1:1:1. It is important to note that although the leaching of CoO and Co\textsubscript{3}O\textsubscript{4} are discussed together in this section, leaching of CoO occurs through a simple displacement reaction whilst Co\textsubscript{3}O\textsubscript{4} also involves the reduction of Co(III) to Co(II). For reference, leaching of Co(II) and Co(III) oxides by HCl proceeds according to the Reactions (1) and (2), respectively, assuming these are solvent independent.\textsuperscript{[19b,c,24]}

\[
\text{CoO} + 2\text{HCl} \rightarrow \text{CoCl}_2 + \text{H}_2\text{O} \quad (1)
\]

\[
\text{Co}_3\text{O}_4 + 8\text{HCl} \rightarrow 3\text{CoCl}_2 + \text{Cl}_2 + 4\text{H}_2\text{O} \quad (2)
\]

These are overall reactions – oxide leaching by acids in aqueous, hydroxylated and solvometallurgical media is considered a multiple-step heterogeneous reaction occurring at the interface of the solid and solution.\textsuperscript{[19b,c]} Leaching of MOs proceeds via the adsorption of the acid onto the oxide surface. If the metal-ligand complexes, for example CoCl\textsubscript{2}, are more stable than the surface metal-OH complexes, adsorbed species may rapidly desorb and/or directly react with the acid (containing a ligand, for example Cl\textsuperscript{−} in HCl) to break the metal-oxide bonds.\textsuperscript{[19b,c]} An important potential advantage of new solvometallurgical systems relative to aqueous media in the leaching of metal oxides is the suppression of hydroxide chemistry for most metals, avoiding the formation of an inhibitory passivating layer during leaching.\textsuperscript{[23]} Acidified hydroxylated solvents are expected to present the same advantageous properties whilst reducing the complexity of the solvent.

For an initial HCl concentration of 0.5 M, 1.0 M and 2.0 M of HCl, diluted in the four hydroxylated solvents, the final dissolved Co(II) concentration starting from CoO oxide is presented in Figure 1b. The same dissolution study using Co\textsubscript{3}O\textsubscript{4} as the cobalt oxide is presented in Figure 1c. All tests were...
performed for a fixed solvent concentration of 90% v/v to account for the difference in water content with increasing HCl concentration. A temperature of 40°C was selected to represent mild treatment conditions, whilst a leaching time of 72 h with vigorous agitation was used to reach equilibrium and neglect potential mass transfer effects arising from the differing solvent viscosities, i.e. the maximum amount of metal that could be dissolved. This time was considered sufficient based on previous comparable studies in which a cut-off of 48 h was used.\textsuperscript{[22]} To illustrate the change in dissolution tendencies between the different solvents and with HCl concentration, the CoO solubility results in Figure 1b were converted to atomic efficiencies in which the stoichiometric ratio between the metal oxide and HCl from Equation (1) was considered to calculate the expected amount of dissolved metal. The same was also performed for Co$_2$O$_3$ dissolution results in Figure 1c according to Equation (2), with all results presented in Figure 1d.

To eliminate the potential contribution of solvent degradation products to the oxide dissolution, the stability of the hydroxylated solvents in the absence of the metal oxides was assessed by $^1$H- and $^{13}$C-nuclear magnetic resonance (NMR) spectroscopy, both in the absence and after mixing with 1.0 M HCl at 40°C for 72 h, shown in Figures S1 and S2 of the Supporting Information. A general shielding of the carbons and protons relative to the pure solvent was observed for all solvents in the presence of HCl, to varying extents. While both $^1$H- and $^{13}$C NMR confirm the stability of EG and BdOH with HCl, as no new peaks are observed, the obtained spectra for Gly and BuOH show some peak shifts in the presence of acid. However, it is unclear if the latter effect is simply due to a change in the local environment of these solvents in the presence of acid or to actual degradation as no new peaks are apparent. Unfortunately, the same analysis after cobalt oxide dissolution is prevented by the paramagnetic nature of Co(II).\textsuperscript{[14]}

Apart from the glycerol system at lower HCl concentrations (0.5 M and 1.0 M), the maximum dissolved concentration of CoO was consistently greater in the acidified organic systems than in the equivalent aqueous leachate as shown in Figure 1b. Whilst a final Co (II) solubility of approximately 0.04 M was obtained for 1.0 M HCl in water, a concentration of 0.13 M Co (II) was obtained for BdOH, and highest for BuOH (0.18 M) and EG (0.19 M), for the same acid concentration. In the case of EG, this represents a nearly fivefold increase in the total dissolved CoO solubility. To illustrate the change in dissolution tendencies between the different solvents and with HCl concentration, the CoO solubility results in Figure 1b were converted to atomic efficiencies in which the stoichiometric ratio between the metal oxide and HCl from Equation (1) was considered to calculate the expected amount of dissolved metal. The same was also performed for Co$_2$O$_3$ dissolution results in Figure 1c according to Equation (2), with all results presented in Figure 1d.

The results depicted in Figure 1b and c indicate the acidified EG and BuOH media as the optimal ones for cobalt oxides dissolution, which is confirmed by their atomic efficiencies (> 36% for 0.5 M and 1.0 M HCl) (Figure 1d). Nevertheless, EG has operational and environmental advantages over BuOH, namely lower cost and toxicity.\textsuperscript{[20a,29]} Considering the importance of cost, toxicity and environmental impacts, Gly and EG would be the most promising of the screened solvents, despite a somewhat lower Co dissolution performance for the former.\textsuperscript{[29,30]} A summary of parameters regarding toxicity, ecotoxicity, cost and environmental impact of the four hydroxylated solvents is available in Table S2.

**General vs. ion-specific solvent contributions**

In the previous section, EG and BuOH were shown to be the most atomically efficient solvents in the recovery of Co, regardless of its valency, for [HCl] ≤ 1.0 M. At these HCl concentrations, the results in Figure 1 suggest an indirect solvent contribution to the leaching. At its simplest, the mean
activity coefficient of ions in solutions is given by the Debye-Hückel equation\[^{[13]}\] in which the activity of the ion is proportional to relative permittivity of the solvent \(\varepsilon\), as well as affected by temperature, ionic strength, and charges. Whilst the validity of this relationship applies only to very dilute solutions, more robust activity models like the Pitzer model contain a Debye-Hückel parameter including \(\varepsilon^{-1.5}\).\[^{[12]}\] If the increased Co oxide solubility observed in Figure 1 is solely due to the effect of solvent on the cobalt cation-chloride anion interactions, then plotting the obtained solubility against \(\varepsilon^{-1.5}\) should yield a straight line, with any significant deviations assigned to ion-specific effects. The resulting plot in Figure 2a yields the expected trend between the solubility in 0.5 M and 1.0 M HCl solutions in all solvents, except for EG. Generally, solvents with lower \(\varepsilon\) than water, in this case all solvents and in the order BuOH (\(\varepsilon = 17.21\)) < BdOH (\(\varepsilon = 28.48\)) < EG (\(\varepsilon = 42.00\)) < Gly (\(\varepsilon = 42.50\)), yielded higher CoO solubility. This is consistent with the previously reported higher activity of the chloride ion in these compounds when compared to aqueous media.\[^{[16]}\] However, the outlier behaviour from EG, especially when comparing its \(\varepsilon\) with Gly (42.00 vs. 42.50), indicates that the enhanced dissolution of CoO in this media is not solely driven by this factor. Upon further comparison between the four solvents, other differences can be noted. When considering ion-specific interactions, such as chelation by the hydroxylated solvents, a higher hydrogenation degree could increase the stability of the metal complexes.\[^{[33]}\] Despite having the same number of hydroxyl moieties as BdOH, EG was able to yield much higher Co solubility than the former. This could be the result of ion-specific interactions between EG and the metal cation, in which the complexation can be achieved in a bidentate configuration, i.e., to form \([\text{Co(EG)}_2\text{(H}_2\text{O})_m]^{2+}\).\[^{[34]}\]

To verify that the increased dissolution of CoO in EG relative to Gly and BdOH is due to the proposed formation of \([\text{Co(EG)}_2\text{(H}_2\text{O})_m]^{2+}\) and not from differences in the chlorocobalt speciation, UV-Vis spectroscopy was used to follow the changes of speciation of cobalt chloride species in each solvent at a Cl : Co\(^{2+}\) molar ratio of 100, as shown in Figure 2b. The source of chloride used was LiCl, to isolate the effect of Cl\(^{-}\) from the acid, when HCl is used. Clear differences between the four solvents were visually apparent, with a change in the pink color and UV-Vis profile characteristic of cationic octahedral complexes \([\text{CoCl(H}_2\text{O})_m]^+\) and \([\text{CoCl(H}_2\text{O})_m]^2+\) to the blue colour of the tetrahedral \([\text{CoCl}_4]^{2-}\) (Figure S3). The cobalt tetrachloride species is more stable in non-aqueous media due to its lower charge density, and therefore Gibbs energy of hydration.\[^{[8,19b,35]}\] A more detailed investigation of the UV-Vis profile with varying Cl : Co\(^{2+}\) molar ratios ranging from 5 to 800 is presented in Figure S4. With increasing Cl : Co\(^{2+}\) molar ratio, a higher ratio of tetrahedral to octahedral cobalt species was observed. The optimal ratio at which mainly the more stable \([\text{CoCl}_4]^{2-}\) would be present changes with the solvent, following the trend with the relative permittivity of the solvents. However, the higher Co solubility in EG without a higher prevalence of cobalt tetra-chloride species supports the conclusion that there is another contribution in the CoO solubility. Considering that the chloride and acid variables have been isolated, the formation of cobalt glycolate complexes is the most likely explanation.

By using lower dielectric, non-aqueous media, cobalt-chloride and cobalt-hydroxy interactions are expected to play a larger role. However, the ion-solvent specific interactions such as the complexes formed with EG confirm that metal dissolution in this media is a complex process. The preceding discussion is based on the dissolution of CoO, with Co\(^{2+}\) being a chlorophilic cation, and must be further nuanced even for other oxides with similar oxidation states and Gibbs energies of formation such as NiO (\(-211.7\) kJ mol\(^{-1}\)) or MnO (\(-362.9\) kJ mol\(^{-1}\)). To briefly illustrate this point, the dissolution of NiO and MnO in 1.0 M HCl in water and the various organic solvents studied is depicted in Figure S5. NiO presented similar solubility trends as those observed for CoO but over 3 times lower under the same conditions, with a maximum of 0.06 M in EG. The differing solubilities can be assigned to the lower stability of the chromonickel complexes and tetrahedral geometry of anionic nickel relative to those of cobalt. As in the case of Co\(^{II}\)), the greater solubility of Ni\(^{II}\)) in EG media is attributed to the formation of

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**Figure 2.** a) Solubility of CoO in 0.5 M and 1.0 M HCl systems according to the relative permittivity \(\varepsilon^{-1.5}\) of each pure solvent at 298 K. A linear regression of these relations, excluding EG (circle points), is depicted as a dashed line. b) UV-Visible (UV-Vis) spectra of CoCl\(_2\) ·6H\(_2\)O in Gly, EG, BdOH or BuOH, with a 100Cl : 1Co\(^{2+}\) molar ratio, with LiCl as the chloride source. A close-up of the differences at the 450-600 nm region is provided as an inset.

The use of strong acids similar to TFMS have been shown to yield high dissolution of cobalt oxides, even in DES. These were assessed and compared to HCl: the "strong" trifluoromethanesulfonic acid (TFMS) and the "weak" lactic acid (LA). These were selected to exemplify two opposite cases of dissociation in aprotic solvents except for BuOH, in which it decreased to 0.39 M. In fact, the residual MnO powder after 72 h dissolution in BuOH changed color from the original green to brown, indicating the oxidation of MnO to Mn₂O₃ and Mn₃(ClOH)₉ as confirmed by X-ray diffraction (XRD) (Figure S6). The oxidation of Mn has been reported as leaching in acidic media occurs, from NMC, as divalent Mn ions react with the surface of the NMC, limiting dissolution after delithiation and an initial leaching stage. The presence of redox reactions prevents the direct extension of the analysis performed in Figure 2 for the non-redox dissolution of CoO to MnO or Co₂O₃.

Influence of acid selection

Having addressed the contribution of the solvent, attention is now turned to the acid selection. Two other acids were assessed and compared to HCl: the "strong" trifluoromethanesulfonic acid (TFMS) and the "weak" lactic acid (LA). These were selected to exemplify two opposite cases of dissociation in aqueous media, namely one for a fully dissociated but non-coordinating acid in TFMS (pKa ≈ 5.9),[17] and one for a partially dissociated acid but excellent metal ligand in LA (pKa ≈ 3.8).[18] HCl (pKa ≈ 5.9) occupies a middle ground as a strong acid providing a mildly complexing counter-anion. In non-aqueous media, the dissociation constants of these acids are slightly lower, being −2.0 and −14.3 for HCl and TFMS respectively.[17] To the best of our knowledge, the pKa of LA in the same organic solvent, dimethyl sulfoxide, has not been reported, but in methanol it was measured as 8.63.[19] Considering the chemical nature of EG, being a protic solvent with a high relative permittivity, the dissociation of these acids is not expected to differ as largely as in a solvent like methanol.[20] The solubility of CoO in 1.0 M of HCl, TFMS or LA in either water or EG, is depicted in Figure 3.

The three acids behaved differently in EG and in aqueous media, as their deprotonation varies according to the solvent. LA resulted in the highest solubility of Co in water (0.07 M) out of the three acids, likely due to the coordination capability of the lactate anion towards the metal. The higher CoO solubility in HCl in water compared to TFMS is likely due to the coordinating nature of the chloride anion.

Interestingly, in EG, the solubility of CoO was similar for both HCl and TFMS within experimental error and significantly higher than in LA (0.04 M of Co). The results for 1.0 M LA in EG are within the same order of magnitude as those reported for the ChCl : EG system upon addition of 1.3 M LA (0.08 M Co).[22] The use of strong acids similar to TFMS have been shown to yield high dissolution of cobalt oxides, even in DES.[20] The Co solubilities values using HCl in this study compared favourably against those in acidic DES despite the significantly lower acid concentration used herein. For example, a cobalt dissolution of 0.13 M was obtained in the ChCl : oxalic acid system at 50°C after 48 h,[21] as well as in the mixture of poly(ethylene glycol) with toluenesulfonic acid DES at higher acid molar ratios.[30]

The different pKa values for these acids in either water or EG can help explain the changes in Co solubilities. HCl and TFMS can be considered to be in their dissociated form in both media due to their pKa values, although they are expected to be slightly more acidic in EG compared to aqueous media. In turn, this contributes to the higher solubility of CoO in EG. In the case of LA, the concentration of free protons and the chelating lactate anion is negatively impacted by the change in solvent from water to EG due to the expected change in the pKa. The low CoO dissolution in water when using TFMS was not expected considering the strength of this acid (pKa ≈ −14.7 compared to −5.9 for HCl) in comparison to HCl in aqueous media. In a work by Pateli et al.,[22] TFMS was combined with a ChCl : EG DES at a concentration 3 orders of magnitude lower than in this work (0.001 M) and less than 0.001 M of CoO was dissolved. They also verified higher solubility of CoO in the same DES with LA, suggesting that importance of the coordination capacity of the organic solvent ligand. That seems to be the case in aqueous media in our work, but not necessarily in EG. The similar CoO dissolution for HCl and TFMS in EG – acids with different degrees of acidity – also suggests that the acidity of the media is not the only driving force to CoO dissolution. The increased CoO dissolution using TFMS in EG compared to water could also have a stabilizing influence from the glycolate ligands. Thus, this further supports the conclusion that other contributions to CoO dissolution play a role in EG, such as the activity of the chloride ion when present.

Care must therefore be taken when extrapolating these results to other non-aqueous solvents, due to different capacity to form complexes with Co ions (e.g., solvation or chelation), as well as otherwise influencing the acid effect. The donor number (DN) of the solvent would help explain an increased solvation of the Co cations, with EG being a stronger Lewis base (DN = 20.7) than water (DN = 16.4).[41]
In summary, the Co dissolution in non-aqueous solvents with superior acid dissociation seems to negatively affect weaker organic acids with coordinating anions. This is consistent with the greater leaching power of DES based on toluenesulfonic acid compared to simple organic acids.\cite{40} However, the acid effect on its own does not seem to drive Co dissolution, with the enhanced Cl− activity in HCl as well as EG complexation with Co cations playing a role. While stronger acids assist Co dissolution, their lower effect on this outcome corroborates the possibility to design less corrosive systems, with reduced dependence on acid content.

The influence of water

Apart from the contribution of acid, either by protons and/or coordinating ligands, and the effect of the solvent, Co dissolution can be further modulated by water content in the solvent mixture. Water is always present in these systems, either originating from the acid or the organic solvent, or from the reactions occurring during metal dissolution. The possibility of using more sustainable versions of these hydroxylated solvents led to assessment of the effect of water content in CoO dissolution. It is relevant to understand how the water content could affect Co dissolution in solvents that yielded variable Co dissolution. For this purpose, different compositions of Gly + water and EG + water mixtures were used to dissolve CoO at a constant HCl concentration of 1.0 M, as depicted in Figure 4.

Within experimental error, the addition of water to EG up to 75% v/v did not significantly impact the CoO dissolution (Figure 4). Further addition of water above 75% v/v to EG results in a sharp decrease in the CoO dissolution to approximately 0.08 M. The decrease in CoO leaching upon water addition is consistent with the hypothesis of EG engaging in stabilizing ion-specific interactions with Co2+. Water dilution could disrupt the Co2+–EG interactions in favor of Co2+–H2O and EG–H2O,\cite{42} thereby decreasing the overall atomic efficiency of the leaching process. Nevertheless, it is worth highlighting that the EG content can be reduced to 25% v/v with minimal loss in the total efficiency, resulting in both environmental and cost savings.

In contrast to the EG system, the CoO dissolution in aqueous Gly mixtures presents an unexpected maximum at 75% v/v water, increasingly linearly from no added water up to 75% v/v and decreasing sharply at 95% v/v water content. The mixture containing 75:25% volumetric fraction of water:Gly yielded the highest observed CoO solubility using 1.0 M HCl (0.27 M Co) with a leaching atomic efficiency of 55% (also higher than the highest value for EG, at 50% efficiency). Considering the extended leaching time used in this study, mass transfer effects (i.e., non-equilibrium conditions) can be rejected as a potential explanation for this surprising behavior. Rather, based on prior computational studies\cite{43} of hydroxylated solvent + water mixtures, it is considered more likely that changes in the solvent’s nano-segregation are responsible for this change. An extended hydrogen-bonded network is formed upon water addition until 75% v/v representing a glycerol molar fraction of xgly = ~0.08 before complete solvation of Gly occurs at 95% v/v water content. At low water content below 25% v/v Gly, Gly keeps its structure with most water molecules dispersed in it, increasing water-Gly H-bonding as water content increases.\cite{44} At water contents around 25% v/v, small water clusters could connect to each other and form a network that facilitates proton transfer, percolation and overall dynamics of the mixture.\cite{45} Thus, any metal dissolution involving these processes could be promoted. This is not the case in EG + water mixtures, EG less affected by water content changes compared to Gly.\cite{46} However, it should be considered that these studies only provide information on the hydroxylated solvent + water mixtures without Co presence. Moreover, the presence of HCl in this work makes it a ternary system and increases the complexity of the potential interactions. For example, it was previously shown that the chloride solvation environment changes from dominated by water or the DES components if water fraction is highest or lowest, respectively. The intermediate compositions resulted in a solvation shell with mixed water and DES components, potentially influencing the chloride activity.\cite{46} Whilst more work is required to elucidate the underlying cause for the observed maximum, the 25% v/v Gly system with stoichiometric addition of HCl stands out as an efficient and environmentally benign leaching solution.

Dissolution of NMC metal oxides in hydroxylated solvents

In NMC cathode materials, the three transition metal oxides are Ni (1+ oxidation state), Co (2+ oxidation state) and Mn (3+ and 4 oxidation state) whilst Li+ is present inter-between the oxide layers.\cite{27} To assess the performance of the two best performing solvent systems – EG (90% v/v EG) and Gly + water (25% v/v Gly) – with NMC matrices, the extraction of Co, Ni and Mn was calculated after leaching from 1:1:1 NMC (LiNi0.33Mn0.33Co0.33O2)
in this media. The leaching of NMC using HCl media can theoretically be described by Equation (3):

\[ 2\text{LiMO}_2 + 8\text{HCl} \rightarrow 2\text{LiCl} + 2\text{MCl}_2 + 4\text{H}_2\text{O} + \text{Cl}_2 \]  

(3)

From Equation (3), a 4:1 HCl to NMC stoichiometric ratio is theoretically required for its total dissolution, with any excess acid added having a negative environmental and economic impact on the leaching process. Thus, to investigate this, the leaching of Co, Ni and Mn from NMC as a function of the HCl to NMC molar ratio was carried out, with the results presented in Figure 5a. The concentration of HCl was maintained at 0.5 M and the quantity of NMC 1:1:1 powder was varied. A HCl concentration of 0.5 M was chosen as it presented the highest atomic efficiency obtained in CoO and CoOCl dissolution although similar results with 1.0 M HCl are also expected.

The extraction of Co, Mn and Ni using different HCl:NMC molar ratios was found to be in accordance with Equation (3), as after the stoichiometric ratio of 4 mol HCl:1 mol NMC was reached, the maximum extraction of the three metals was achieved (Figure 5a). For Co and Mn, 100% extraction was obtained, while Ni levelled off at around 94% extraction, in both EG and 25% Gly media. Similar maximum leaching values for the three transition metals in NMC has been reported, due to their lattice structure, where the three metals are in a layered oxide.[36,47,48] Although useful, these leaching values do not provide complete information about their dissolution mechanism, which requires further studies. For instance, kinetics studies provide information on the limiting steps of the reaction.

To further understand the kinetics of the extraction of Co, Mn, and Ni from NMC, this process was assessed over time and at three different temperatures, 25 °C, 40 °C and 60 °C (Figure 5b). The amount of HCl was kept above the stoichiometric ratio from Equation (3), using around 6 mol HCl:1 mol NMC at all temperatures, to ensure maximum dissolution. Co and Ni were co-extracted, maintaining a similar profile throughout the full extraction process, and being extracted to a lower extent than Mn (≈62% Co and Ni vs. ≈93% Mn, at 25 °C).[47]

Considering the results from the previous section, Mn extraction could have been affected by a different mechanism, resulting in its higher dissolution compared to Co and Ni. A difference in mechanism between Mn and Co during the acid leaching of NMC was previously reported, with a Mn-rich shell formed in earlier leaching stages on the NMC particle, covering the bulk that also contains Co and Ni, affecting subsequent leaching.[36] A similar preferential leaching was observed at 40 °C, but was attenuated at 60 °C where Co and Mn presented a comparable leaching efficiency, with 96% Co extracted and 100% of Mn, and 85% of Ni. Total leaching was attained in 8 h at 60 °C, as opposed to lower temperatures where Co and Ni were less than 49% extracted and 63% of Mn (at 8 h, 25 °C). At higher temperatures, the degradation of the organic solvents could occur,[36] with a trade-off between extraction time and temperature being required when considering an industrial application.

The kinetic experiments from Figure 5b were used to prepare Arrhenius plots in the temperature range of 25 to 60 °C. The shrinking core model is commonly used[46,49,50] to assess the leaching mechanism of Li-ion active cathode materials,[51] being described by Equations (4) and (5), for a process controlled by diffusion or by surface chemical reactions, respectively. In both cases, x is described by the leaching efficiency, in percentage, k the reaction rate constant (h⁻¹), and t the reaction time.

\[ 1 - \frac{2}{3}x - (1-x)^{\frac{3}{2}} = kt \]  

(4)

\[ 1 - (1-x)^{\frac{3}{2}} = kt \]  

(5)

The plots of these equations for Co, Ni and Mn are depicted in Figure S7, with the parameters used for the kinetic models reported in Table S3. The reaction rate constant, k, was used, along with the temperatures, to determine the apparent activation energies (E_a) of each metal leaching, according to the Arrhenius equation [Eq. (6)].

\[ k T = A e^{-E_a/RT} \]  

(6)
\[ \ln k = \ln A - \frac{E_a}{RT} \]  

(6)

Considering the linear fits provided by each kinetic model, being a diffusion- or surface-controlled reaction, in Figure S7, it seems the dissolution process of the three metals across the three studied temperatures is best described by a diffusion-controlled process \((R^2 \geq 0.74)\), especially for Mn \((R^2 \geq 0.94)\). Nonetheless, the \(R^2\) values from Table S3 suggest that the diffusion-controlled model does not fully depict the leaching of Co and Ni from the NMC matrix during the full dissolution process, as they correspond to poor fittings in some points. For these metals, the reaction could be better represented by other models, or even different models at different stages. For example, redox reactions could occur during the dissolution process, not following the shrinking core mechanism. An alternative model, the logarithmic empirical, has been proposed\(^{[50]}\), being described by Equation (7). Similarly, a mixed model comprising both diffusion- and surface reaction-controlled components could be in place,\(^{[51]}\) being described by Equation (8).

\[ [-\ln(1-x)]^2 = kt \]  

(7)

\[ \frac{(1-x)^2 + 1}{3} \ln(1-x) = kt \]  

(8)

The plots for the fittings using Equations (7) and (8) are in Figure S8, with the kinetic parameters being summarized in Table S3. Indeed, these models were on par with the diffusion-controlled model as better representations of the Ni leaching kinetics than a surface-controlled mechanism \((R^2 \geq 0.83)\). For Co, the fits were better at 25 °C and 40 °C \((R^2 \geq 0.91)\) but not for 60 °C \((R^2 \geq 0.58)\). Such is in line with the hypothesis that there are multiple contributions in the overall dissolution process, as discussed in the previous sections, as there was no clear dominant control. For further clarification, a description of the Co and Ni leaching kinetics considering a two-step process was tested for the shrinking core diffusion- and surface reaction-controlled models, being summarized in Figure S9 and Table S4. From these, it is clear the Co and Ni leaching best defined as a diffusion-controlled process in the initial stage (up to 4 h, \(R^2 \geq 0.96)\). Regarding the second step of leaching, there was no clear preference of kinetic model. Thus, these results are in accordance with the presence of a mixed-controlled leaching mechanism of Co and Ni from a NMC matrix using 0.5 M HCl in 25 % Gly/water.

The resulting Arrhenius plots for the leaching of the 3 metals are depicted in Figure 6. Considering the previous model fittings, the mixed-controlled kinetic model was applied for Co and Ni, while a diffusion-controlled process was considered for Mn. From these, the apparent activation energies \((E_a)\) are 87 kJ mol\(^{-1}\) for Co, 60 kJ mol\(^{-1}\) for Ni and 50 kJ mol\(^{-1}\) for Mn. The higher activation energies for overall dissolution of Co and Ni indicate that this process is chemical reaction-controlled (usually above 40 kJ mol\(^{-1}\) in these processes\(^{[55]}\)), while Mn has the same limitation but is more easily dissolved.\(^{[49,54]}\) These results support the conclusion that the dissolution of Co and Ni is limited by the rate of the chemical reactions, likely both with HCl and the solvent. It is worth highlighting that the fitting correlation for the \(E_a\) of Co and Ni arise from a poor fitting of the mixed-controlled model at 60 °C \((R^2 \geq 0.6)\) such that the obtained \(E_a\) should be regarded as semi-quantitative, although they are consistent with the hypothesis that chemical reactions play a larger role in limiting the rate of reaction.

The lower activation energies for Mn dissolution relative to Co and Ni are consistent with the highest dissolution of Mn(II) when the metals were studied individually in Figure S3, as well as the leaching efficiency depicted in Figure 5b. Nevertheless, the reported activation energies for NMC leaching using HCl in hydroxylated solvent are lower than the comparable aqueous system. The dissolution from a 1 : 1 : 1 NMC in 4 M HCl has been reported to have activation energies of around 100 kJ mol\(^{-1}\) for Co, Ni and Mn, with the surface chemical reaction controlling the leaching process.\(^{[50]}\) Although lower activation energies of 28 kJ mol\(^{-1}\) for Co from a lithium cobalt oxide (LCO) LIB were reported using 3 M HCl,\(^{[55]}\) such required the use of H\(_2\)O\(_2\) as a reducing agent. Without H\(_2\)O\(_2\), but still using 2 M HCl, the calculated activation energy rose to 48 kJ mol\(^{-1}\) in a two-step leaching of Co from LCO.\(^{[56]}\)

The indication of lower activation energies for the dissolution of Co, Ni and Mn in this work compared to previous works pave the way for a system that besides being greener, due to lower acid content and use of milder chemicals, could also be more efficient than conventional media. Nonetheless, this is only a starting system towards obtaining simpler and completely green LIB recycling processes.
Conclusions

Four hydroxylated solvents, glycerol (Gly), ethylene glycol (EG), 1,3-butenediol (BdOH) and 1-butanol (BuOH), were screened for their use as dilute HCl media to dissolve Co oxides with different oxidation states, CoO and Co$_3$O$_4$. The EG solution yielded the highest CoO solubility ($>$0.19 M Co) which was higher than the deep eutectic solvent (DES) containing these solvents as their components. This was attributed to increased chloride activity in this media and beneficial solvent-specific interactions. While acidity was necessary and promoted Co oxides dissolution, the chloride activity seemed to be a contributing factor in achieving the highest solubility, being higher in non-aqueous media. Similar trends were noted for Co$_3$O$_4$, and the EG–Co specific interactions were also proposed, including for NiO dissolution. Mn was more soluble than other metals (0.50 M Mn) across all solvents except BuOH, likely due to a different, redox-based mechanism.

Compared to other acids, HCl was more efficient in EG media than coordinating ligands from lactic acid (LA) and a strong acid such as trifluoromethanesulfonic acid (TFMS), despite the weaker strength than in aqueous solutions, due to solvent contributions. A less acid-dependent media, with HCl diluted in 25% Gly (v/v) and water, yielded the highest Co dissolution (0.27 M Co), attributed to a change of the H-bonded network, affection ion solvation and ligand availability. The same enhancement was not found for EG + water media, further supporting the importance of EG-metal interactions in metal dissolution.

Generally, enhanced dissolution of Co, Ni and Mn oxides occurred as a result of multiple contributions, such as the chloride activity, solvent-specific interactions, acidity, and solvent structure. The application of the best two solvent systems to a commercial nickel manganese cobalt (NMC) cathode material was effective, with 100% extraction of Co and Mn and 94% of Ni in 0.5 M HCl in Gly (O) compared to 84% in water media. Further, the use of 25% Gly (O) + 0.5 M HCl increased the extraction of Mn from the NMC cathode powder to 97%, while the purity of the extracted Mn was 94%. The application of this approach as coupled with other strategies, such as electrochemical or solvometallurgical recovery of metals, has shown promise as a promising method for the sustainable hydrometallurgical recycling of lithium-ion batteries (LIBs). This is envisioned by coupling this approach with other strategies, such as electrochemical or solvometallurgical recovery of metals. These can be used not only to reduce the environmental impact of the overall process, but also to improve the leaching efficiency and selective recovery of metals.

Experimental Section

Chemicals and instrumentation

A detailed description of the chemicals as well as the sample analysis methodology used in this work can be found in the Methodology section of the electronic Supporting Information.

Metal oxide dissolution and characterization

Acidic aqueous and hydroxylated solvent systems were gravimetrically prepared by careful weighing each component using a Sartorius Practum (uncertainty ±0.0001 g) analytical scale and mixing them in a sealed container until a homogeneous solution was obtained. The compositions assessed in this work are summarized in Table S1. In hydroxylated systems, the water content (v/v%) was determined including both the added water as well as the implicit water introduced from the use of acid, increasing with acid concentration in the case of 37 wt.% HCl for example.

The solubility of each metal oxide (MO) in the solvent systems was determined by preparing a saturated MO solution in 1 mL of each solvent system. An initial 20 mg of MO was initially measured into the flask, with more MO added if complete dissolution was attained. The solutions were centrifuged at 10,000 rpm for 10 min, with the supernatant recovered and filtered using a nylon syringe filter with a pore size of 0.22 μm prior to quantification. Metal concentrations were determined using a Picoflex S2 (Bruker, Germany) total reflection X-ray fluorescence (TXRF) spectrometer, with a molybdenum X-ray source operating at 50 kV. In each graph, the error bars represent the standard deviation of the experiment considering at least 2 separate measurements.

Metal extraction from NMC using hydroxylated solvents

The extraction of Co, Ni and Mn from a representation of NMC 1:1:1 active cathode material was determined in 0.5 M HCl in either EG or 25% Gly (v/v) + water. The extraction efficiency was calculated according to Equation (9), with $C_i$ and $C_{i, \text{initial}}$ corresponding to the concentration of metal $i$ in the leachate and in the initial NMC powder, respectively.

$$\% \text{ Extraction} = \frac{C_i(t)}{C_{i, \text{i, initial}}} \times 100 \tag{9}$$

Following a similar procedure as that described for simple MO dissolution, leaching was carried out for a fixed HCl to NMC molar ratio using a continuous stirring at 2,000 rpm and 40°C for 72 h. After this process, the solutions were centrifuged at 10,000 rpm for 10 min, filtered and the metal content was determined using TXRF after dilution. For kinetic studies, the NMC was continuously stirred in 0.5 M HCl in 25% Gly (v/v) + water at 2,000 rpm at either 25°C, 40°C or 60°C up to 48 h. At different times, the stirring was briefly stopped, and an aliquot was removed from the top layer of the solution, with the metal content being determined by TXRF as previously described.
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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: battery recycling · deep eutectic solvents · metal dissolution · sustainable chemistry · transition metals


[49] W. Xuan, A. de Souza Braga, C. Korbel, A. Chagnes, Hydrometallurgy 2021, 204, 105705.


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A puzzle piece of 'greener' battery recycling: Hydroxylated solvents were used with low concentrations of HCl to effectively dissolve metals – Co, Ni and Mn – and shed light on their dissolution mechanism in complex systems. The potential for simpler yet 'greener' systems than conventional hydrometallurgy was demonstrated by using high water fractions in metal dissolution.

Enhanced Dissolution of Metal Oxides in Hydroxylated Solvents – Towards Application in Lithium-Ion Battery Leaching

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