Enhanced dissolution of valuable metal oxides from spent lithium-ion batteries in sustainable alcohol-based solvents

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Introduction

The road to decarbonization and technological evolution relies on energy storage systems, such as Li-ion batteries, **increasing the demand for their constituting metals**.[1] The recovery of these metals requires more sustainable approaches,[2] such as **ionic liquids and deep-eutectic solvents** which can provide **higher selectivity** and sustainability, despite having disadvantages which could be mitigated by simple systems, such as alcohols.[3]

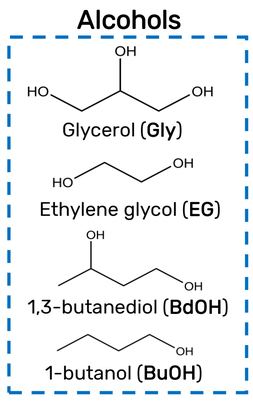
Objectives

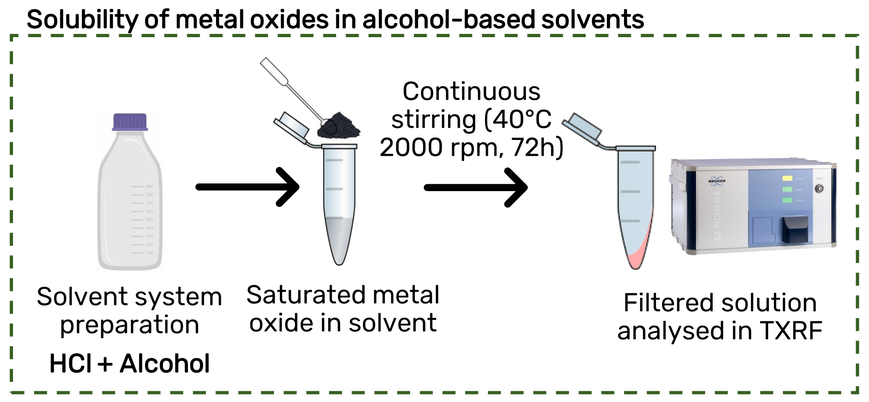
Improve the understanding of **how alcohol-based dilute acid solutions enhance metal dissolution**.

Apply these as **more sustainable and simple systems** for metal leaching processes.

Methodology

CoO, **NiO** and **MnO** dissolution was assessed in **dilute HCl alcohol solutions** and quantified using total reflection X-ray fluorescence spectrometry (TXRF).





Metal oxide dissolution in alcohol-based solvents

1 CoO dissolution

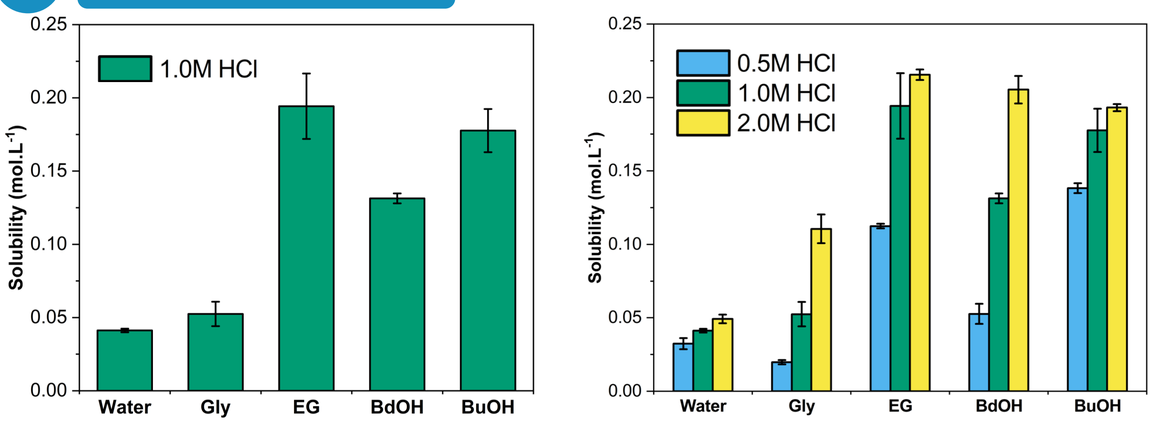


Fig.1. Solubility of CoO in 0.5M, 1M or 2M HCl aqueous or alcohol-based solutions (90% v/v), after dissolution for 72h at 40°C and 2000 rpm.

Higher CoO solubility in alcohol-based media compared to aqueous solutions (EG > BuOH > BdOH > Gly > Water)

Co is a chlorophillic metal → Solubility consistent with **higher Cl^- activity in alcohols**[4]

CoO solubility increase with [HCl]

Due to higher proton activity

Required for metal oxide dissolution

$$CoO + 2\,HCl \rightarrow CoCl_2 + H_2O$$

$$CoCl_2 \rightarrow [CoCl_4]^{2-}$$

Continuous Cl^- coordination with Co yields a more stable species,[5] $[CoCl_4]^{2-}$

2 Alcohol effect

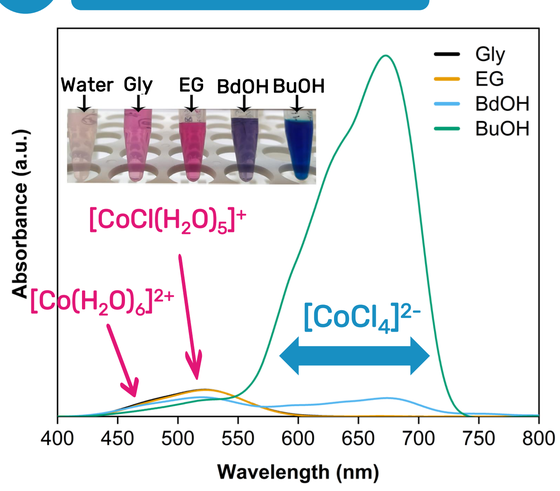


Fig. 2. UV-Vis spectra of $CoCl_2{\cdot}6H_2O$ in each alcohol with 100 Cl^- : 1 Co^{2+} molar ratio.

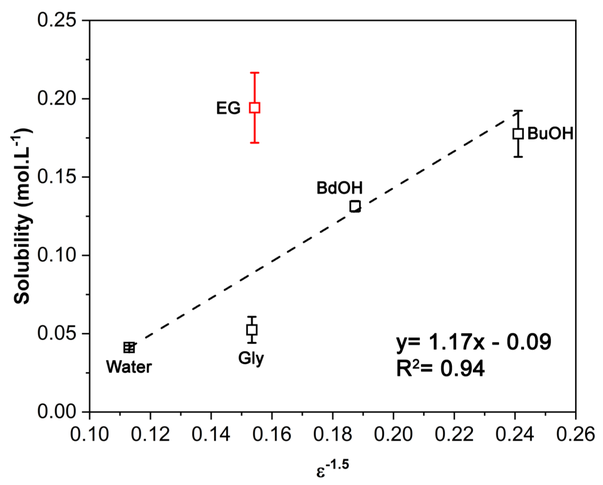


Fig. 3. UV-Vis spectra of $CoCl_2{\cdot}6H_2O$ in each alcohol with 100 Cl^- : 1 Co^{2+} molar ratio.

Varying Co speciation despite same [Cl^-] → **Cl- activity is different in each alcohol**

Based on the Cl^- activity determination, **Cl- activity increases with lower ε**[6], **except for EG**, possibly due to ion-specific interactions

3 Water presence and H-bonding

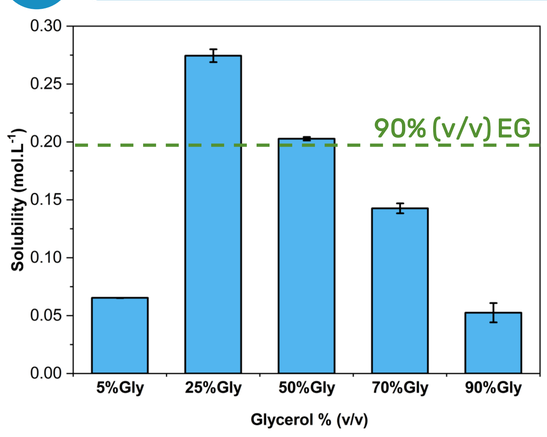


Fig. 4. Solubility of CoO in 1M HCl in water/glycerol mixtures, according to **Gly v/v %**.

The red-shift in **O-H stretching** indicates higher H-bonding[7]

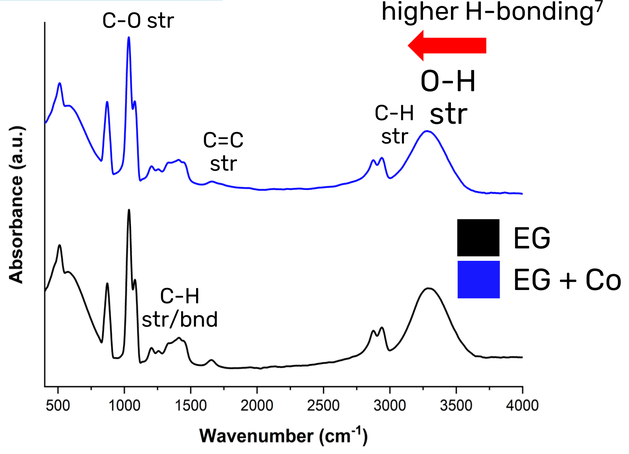


Fig. 5. FTIR spectra of pure EG and resulting solution from CoO dissolution in 1M HCl in EG.

Highest Co solubility in 25% (v/v) Gly/Water mixtures → **Increased H-bonding** and molecular organization changes → Could occur through H^+ adsorption, **promoting Cl^- coordination**[7]

4 Comparison with NiO and MnO

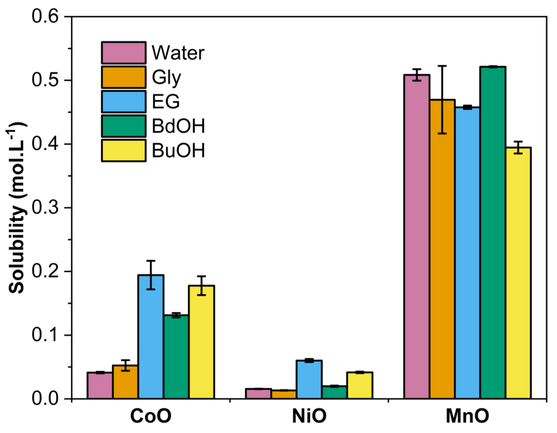


Fig. 6. Solubility comparison of CoO, NiO and MnO in 1M HCl solvent systems.

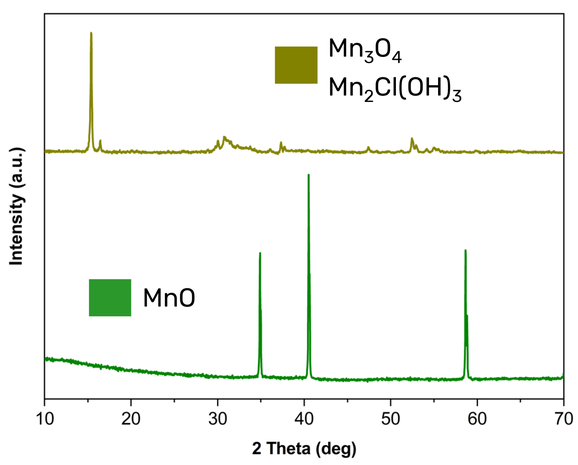


Fig. 7. XRD pattern of MnO and the resulting solid after dissolving MnO in 1-butanol.

MnO has the **highest solubility** ↑ 7.7x Ni, 2.4x Co

CoO more soluble than NiO ↑ 3.2x Ni

Oxidation state differences after dissolving MnO may indicate a different dissolution mechanism

Conclusions

- CoO **dissolution is enhanced in dilute HCl alcohol-based media** compared to aqueous media with the same [HCl], due to **increased Cl^- activity** in this media;
- **HCl in EG was the media with highest CoO dissolution**, exceeding that expected from the Cl^- activity in this media;
- Water content may result in higher metal oxide dissolution through **increased H-bonding and H^+ adsorption on alcohols**;
- **CoO seems to be dissolved preferably over NiO**, due to its chlorophilicity;
- **MnO is the most soluble** metal oxide, regardless of the media used, possibly due to a different dissolution mechanism.

References & Acknowledgements

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