Supplementary Information

Solvometallurgy: Design of Ternary Deep Eutectic Solvents for the Electrochemical Recovery of Nickel from Lithium-Ion Cathode Materials

Suchithra Ashoka Sahadevan,^[a] Mohamed Shahid,^[b] Shrihari Sankarasubramanian,^[b] Vijay Ramani*^[a]

*Corresponding author e-mail: ramani@wustl.edu

1. Experimental

Materials and methods.

Materials: Choline chloride (ChCl) (99%), Ethylene glycol (EG) (99%), NiCl₂·GH₂O (98%), Nitric Acid, and Lithium nickel oxide (LNO, 97%), Poly (vinylidene fluoride) (PVDF), and N-Methyl-2-pyrrolidone were purchased from Sigma Aldrich. Citric Acid (CA) (anhydrous, 99%) (Fisher) was used as received. ICP standards of Li and Ni (1000 µg/mL) were obtained from Aldrich. All the chemicals were used as received without any further purification. Deionized water (di-water) was used to prepare DES.

Synthesis. DESs were prepared by mixing and heating the three components, ChCl, EG, and CA, in a 200 ml glass bottle. ChCl served as HBA; EG and CA were HBD and used as obtained. The ChCl, EG, and CA were mixed in a 1:2:1 molar ratio and were heated to 85 °C while stirring at 200 rpm until a transparent viscous liquid was formed. The DES mixture was cooled to room temperature and stored in a desiccator for further use.

Characterization. The conductivity of DES at different temperatures was measured using electrochemical impedance spectroscopy (Solartron analytical potentiostat (1470 Cell test system) connected to a 1252A Frequency Response Analyzer). Conductivity measurements were carried out in a low-volume three-electrode electrochemical cell (Pine) with a volume of 6 mL solution and two glassy carbon (GC) electrodes (0.3 cm diameter) separated by a distance of 0.4 cm. The collection of impedance spectra was in the frequency range of 0.1–30,000 Hz with an amplitude of 10 mV of the AC signal. Conductivity was calculated using the following equation:

$$\kappa = \frac{l}{RA} \tag{5}$$

Where κ is conductivity in Siemens per centimeter (Scm⁻¹), I is the distance between electrodes, A is the cross-sectional area of the sample, and R is resistance (Ω).

Thermogravimetric analysis (TGA) was used to evaluate the thermal stability of DES and its components, and the results were determined using a TGA Q5000 instrument. The temperature was ramped up from 300 to 850 K at a heating rate of 10 $^{\circ}$ C·min⁻¹ under nitrogen flow. The first derivative of weight as a function of temperature was used to identify the maximum degradation temperature. TGA data were recorded with a heating rate of 10 $^{\circ}$ C/min in N₂ flow. The Fourier transform infrared (FI-IR) was obtained with a spectrometer (Thermo-Scientific NICOLET iS-50) using an attenuated total reflectance (ATR) sampling mode with a germanium crystal. The complete spectrum between 4000–800 cm⁻¹ was recorded as an average of 32 scans at a resolution of 4 cm–1. Ultraviolet-visible (UV-VIS) spectra of DES leach liquor at 298 K and 358 K were measured using a Shimadzu model spectrophotometer connected to a chiller with a quartz cuvette cell. 121 CEC DES was used as the background. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) analyses were conducted to obtain surface morphological and elemental information of the electrodeposited substrates. All images were acquired by an FEI XL-30 series instrument equipped with an Oxford X-Max SDD (Silicon Drift Detector) 20 mm² EDS system using secondary electrons at an accelerating voltage of 5 kV.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed using Thermo iCAP 7400 Duo, and Cetac ASX-560 autosampler, controlled by Qtegra software, was used to determine metal concentrations. Calibrations were performed using Ni and Li ICP grade standards 1000 mgL⁻¹ (Merck), diluted using 2% nitric acid. Scandium was used as the internal standard. To negate the effect of organic content in DES on the IC-OES measurements, dilution was chosen as 1000. Each mass-based metal concentration is the average of at least three measurements.

Leaching of LNO. 0.1 g LNO and 5 g DES were mixed in a 20 ml glass vial equipped with a magnetic stirrer in an oil bath for 24 h. Leaching experiments using 121 CEC DES were conducted at various temperatures (323, 343, 367, and 383 K) for 24 h. All experiments were performed at least in triplicate. The metal concentrations were analyzed using (ICP-OES).

For the time optimization of the leaching process, intermediate samples (~0.1 g) were taken at certain time intervals. The samples were immediately diluted with di-water (around 100 times the mass of the collected sample) for ICP-OES analysis and filtered with syringe filters (Fischer, pore size 0.22 μ m, polypropylene) and were further diluted using 2 % HNO₃. Leaching of LNO with 12 CE was also carried out for one leaching condition (363 K for 24 h). The LE of metals was calculated using the following equation: (2)^[1]

$$LE (\%) = \frac{Y C_i M_1}{M_0 w_i} x100$$
(6)

Where Y is the dilution factor of DES leachate by di-water, C_i is the metal ion (Li, Ni) concentration in water obtained from ICP-OES (mg/kg), M_i is the mass of the DES leachate (kg); M_0 is the mass of LNO (mg) and w_0 mass fraction of metal in the cathode material.

Electrochemical measurements. Cyclic Voltammetry (CV) was performed using a solartron potentiostat controlled by Corrware software. In an electrochemical cell, a three-electrode system was used, consisting of a GC with a surface area of 0.1963 cm² as working electrode (WE), a platinum wire as counter-electrode (CE) and a silver wire as quasi-reference electrode (RE). The WE was polished with 0.05 µm alumina and cleaned by di water rinsing and isopropanol. All CVs were recorded at 358 K unless specified. The platinum electrode was sonicated in DI water, dried, and heated in a hot flame to remove oxides. The silver wire was polished with sandpaper, washed with DI water, and dried. All CV measurements were performed at 358 K unless otherwise specified.

CV of leachate solution: CV was conducted using approximately 30 mL for each measurement at 85 °C. Between experiments, the GC electrode was thoroughly cleaned. Due to the solution's high viscosity and hydrophilic nature, careful handling was required. To ensure solution homogeneity, the leachate was stirred before each experiment and allowed to rest before measurements. The GC (0.196 cm²), RE, and WE electrodes were positioned as close as possible to minimize potential drops and improve measurement accuracy. The open-circuit potential (OCP) was recorded for at least 5 minutes or until stabilization (~0.4 V) was achieved. Between the experiments, OCP is expected to remain constant. CV scans were recorded at a scan rate of 20 mV/s, with the potential swept from 0.5 V vs Ag to the cathode end potentials. Due to the complex nature of the solution, surface interactions, and batch-to-batch variations in water content in leachate solution, only qualitative trends from the CV data were analyzed. Additionally, 2 mL of water was added to the leachate to reduce viscosity, and the resulting electrochemical response was compared.

Additionally, CV of citric acid was performed at different concentrations (0.05 M, 0.5 M, and 2 M) using GC as the WE, Pt as the CE, and Ag/AgCl as the RE at RT.

Electrodeposition: Ni electrodeposition was carried out in a three-electrode setup with a 100 ml solution. Copper (Cu) foam, Cu sheet, or carbon paper was used as WE, stainless steel (SS), or ruthenium iridium oxide coated on titanium (RTI) support as CE, and Ag wire as RE. The Cu sheets and foam were mechanically polished using 600-grit sandpaper. Subsequently, the substrates were cleaned in di-water and acetone and dried in an oven for 5 minutes. The WE area was maintained between 4–7 cm², parallel to the CE, while the RE was positioned closer to the WE.

Electrodeposition was carried out at 358 K for 30 min. After deposition, the WE was rinsed with DI water and dried with acetone at 60 °C for about 5 min. The amount of Ni deposited was determined by weighing the WE before and after the experiment. FE and RNi were calculated using Equations (7) and (8).

$$FE (\%) = \frac{w \, x \, n \, xF}{Q \, x \, M} x100 \tag{7}$$

$$R_{Ni} \left(mg \, h^{-1} cm^{-2}\right) = \frac{w}{A \, x \, t} \tag{8}$$

Where w is the weight of the Ni deposited, n is the number of electrons transferred (in this case n=2), M is the molar mass of Ni (gmol⁻¹), F is the Faraday's constant (96,485 Cmol⁻¹), Q is the overall charge (C), A is the area of the substrate (cm²), t is the electrodeposition time (h).

Chronoamperometry measurements were conducted in leachate solutions at varied temperatures utilizing a GC (0.071 cm^2) as the WE, Pt as the CE, and Ag wire as the RE. The potential was initially set at a potential of 0 V for 10 s, where no faradaic current was observed, and subsequently stepped to potentials -1 V to -1.6 V vs Ag wire, where Ni deposition began. The current density-time curve was

performed for different potentials (-1 V, -1.2 V, -1.4 V, and -1.6 V) at 358 K.^[2] The j-t transients indicate a rise in current density, reaching a maximum value J_m at time t_m , and then further decreases in current density.

$$Q = \frac{2nFAC\sqrt{Dt}}{\sqrt{\pi}} + Q_{dl} + Q_{ad}$$
(9)

Where Q is the charge (C); n is the number of electrons transferred; A is the area of the planar electrode (cm²); C is the concentration of Ni ions in leachate solution (mol/cm³); D is diffusion coefficient (cm²/s); t is time (sec); Q_{dl} and Q_{ad} are charge contributions due to the charging of electrical double layer and adsorbed species on the electrode surface.

Reusability of DES. DES was subjected to optimum leaching conditions (90 °C, 4h) followed by electrodeposition conditions (115 °C, -1.4 V, 30 min) called cycle 1. After completing this process, 5 g of the treated DES was combined with 0.1 g of LNO and subjected to the same leaching conditions (90 °C, 4 hours). The leaching efficiency (LE) was then determined using ICP-OES. DES collected after cycle 1 was subjected to the same leaching and electrodeposition conditions, called cycle 2. Leaching studies were then performed with DES collected after cycle 2.

Simulated black mass. A simulated black mass was prepared by thoroughly mixing 80 wt% commercial LNO, 10 wt% PVDF, and 10 wt% Super P carbon with N-Methyl-2-pyrrolidone solvent. The mixture was homogenized, and the resulting slurry was evenly spread over a glass sheet. After drying, the simulated black mass was recovered for leaching.

2. Characterization of T-DES

2.1 Aqueous citric acid vs Citric acid-based DES

We compared the metal recovery using aqueous CA (aq. CA) (hydrometallurgy) and CA-based DES (121 CEC; solvometallurgy) in terms of leaching and electrodeposition parameters.

Leaching: Aq. CA solutions achieve over 90 % LE for Li and Ni. Higher temperatures, concentrations, and additional reducing agents (e.g., H₂O₂) further improve LE (Table S3).^[3,4]

ESW: The 121 CEC DES offers a wider and more stable ESW (2.55 V vs. Ag wire) compared to aq. CA (1.8 V vs. Ag/AgCl), making it more suitable for electrodeposition (Figure S1, S8-S9). In aq. CA, the ESW decreases with increasing concentration and temperature, with a 2 M solution showing a cathodic onset potential of 0.2 V vs. Ag/AgCl at 298 K, leading to side reactions during Ni²⁺ reduction (~-0.25 V vs. Ag/AgCl). At higher temperatures (358 K), the cathodic onset potential in aq. CA decreases further to 0 V vs. Ag/AgCl. (Figure S21). Despite the higher viscosity of DES, it maintains a stable ESW at elevated temperatures, enabling more selective and efficient metal recovery. Future work should focus on designing low-viscosity DES with stable ESW for further progress in solvometallurgy.

Cathode material	LE (%)	Citric acid concentration	Leaching conditions	ref	
		(additional reducing agent)	(Temperature (K);		
		(M)	Time (min)		
LNMCO	90 % Li, 91 % Mn, 93% Co,	1.5	343 K, 1440 min	[5]	
	92 % Ni, 78 % Al				
LNMCO	95 % Co, 97 % Li, 99 % Ni	1.5	368 K, 30 min	[3]	
LCO	100 % Li, 91 % Co	2 (0.6 M H ₂ O ₂)	363 K, 30 min	[6]	
LCO	100 % Li, 80 % Co	0.1 (0.02 M ascorbic acid)	353 K, 360 min	[7]	
LCO	100 % Li, 90 % Co	1.5/9.8 M H ₂ O ₂	363 K, 30 min	[4]	
$6H^{+}_{(CA, aq)}+2LiMO_{2(s)}+H_2O_{2(aq)}\rightarrow 2Li_3^{+}_{(citrate,aq)}+2M_3(citrate)_{2(aq)}+4H_2O+O_{2(q)}[M=Co, Nietc)$					

Table S1: LE of metals from various cathode materials using aqueous citric acid solutions under different leaching conditions.



Figure S1: (left) CV profiles of citric acid aqueous solution at RT for different concentrations (0.05 M, 0.5 M, 2 M) using GC as WE, Pt as CE, and Ag/AgCl as the RE. The inset image shows the magnified view in the potential window between 0.4 V and -0.45 V vs Ag/AgCl. (right) CV profiles of 2 M citric acid aqueous solution at different temperatures (298 K, 328 K, and 358 K) using GC as WE, Pt as CE, and Ag/AgCl as the RE. The inset shows a magnified view of the CV curves at lower potentials between 0 V and -0.8 V vs Ag/AgCl. Scan rate 20 mv/s.

FT-IR: The 3200–3500 cm⁻¹ peak indicates N-H/O-H stretching bands in ChCl, EG, and CA. The peaks around 3000-2800 cm⁻¹ in EG correspond to C-H, CH₃, and CH₂ stretching bands, and the presence of the same peaks in 121 CEC confirms the presence of EG. The two peaks around 1743 and 1686 cm⁻¹ can be attributed to carbonyl stretching bands ν (C=O) from carboxylic acid groups of CA. However, in the case of 121 CEC, only one peak is observed in this region, possibly due to the formation of new hydrogen bonding. The presence of amide band II (ν (C-N)+ δ (N-H)) around 1500 cm⁻¹ and C-Cl stretching bands around 600-500 cm⁻¹ in ChCl and T-DES, confirm the presence of ChCl in 121 CEC. ^[8–10]





Figure S2: a) Chemical structure and different molar combinations of CEC. b) FT-IR of 121 CEC and precursors.

Viscosity and conductivity

$$\ln \sigma = \ln \sigma_o - \frac{E_a}{RT} \tag{10}$$

where, σ is the conductivity (mS cm⁻¹) at temperature T (K), σ_0 is the conductivity (mS cm⁻¹) at a reference temperature T₀ and E_a is the activation energy (kJ mol⁻¹) for the ion conduction.



Figure S3: (left) Viscosity and conductivity of 121 CEC as a function of temperature. The error bars represent standard errors calculated from three independent experiments. (right) Temperature-dependent conductivity of the 121 CEC represented in an Arrhenius plot. The error bars represent standard errors calculated from three independent experiments.

Thermal stability



Figure S4: a) TGA and b) derivative of 121 CEC and precursors.



Figure S5: LE of Li and Ni using 121 CEC for varied temperatures (323-383 K) for 24 h. The error bars represent standard errors calculated from three independent experiments.

3. Leaching kinetics:

Film diffusion-controlled process	x = kt	(11)
Chemical reaction-controlled process	1	(12)
	$1 - (1 - x)^3 = k_r t$	
Product layer diffusion-controlled process	$2, \frac{2}{2}$	(13)
	$1 - \frac{1}{3}x + (1 - x)^3 = k_d t$	
Mixed control reaction	1 1	(14)
	$1 - (1 - x)^3 - \frac{1}{3} \ln (1 - x) = k_M t$. ,
Avrami model	ln[-ln1-x) = lnk + nlnt	(15)
e leached metals, kr, kd, and kM are the chemical r	reaction rate constant, diffusion-reaction	rate constant,

Where x is the leached metals, kr, kd, and kM are the chemical reaction rate constant, diffusion-reaction rate constant, and mixed control reaction rate constant (min⁻¹), and t is the leaching time (min).

The activation energy was calculated using the Arrhenius equation:

 $K = A \cdot e^{-Ea/RT}$

Temperature (K)	Chemic control	al reaction- led process	Diffusion	n controlled action	Mixed	l control	Avrami	model
Li	R ²	к	R ²	к	R ²	к	R ²	ln K
343	0.90	0.0033	0.96	0.0011	0.92	0.00776	0.99	-3.99
363	0.78	0.0043	0.93	0.0017	0.88	0.01217	0.97	-1.81
383	0.94	0.0076	0.95	0.003	0.93	0.0234	0.99	-1.71

Where A is the Arrhenius constant, Ea is the activation energy of the reaction, R is the universal gas constant, and T is the temperature (K).

Table S2: R^2 and rate constant of Li fitted in equations 12 and 15.

Temperature (K)	Chemical reaction- controlled process		Diffusion controlled reaction		Mixed-control		Avrami model	
Ni	R ²	к	R ²	к	R ²	К	R ²	ln K
343	0.89	0.0047	0.96	4.33x10 ⁻⁴	0.98	0.0045	0.93	-2.22343
363	0.85	0.0037	0.98	0.0013	0.90	0.0087	0.97	-1.276
383	0.98	0.0021	0.96	0.0018	0.92	0.0117	0.89	-1.522





Figure S6: Arrhenius plot for Li and Ni, obtained by fitting the slopes of equation 13 of diffusion-controlled reaction.



Figure S7: UV-VIS of a) NiCl₂.6H₂O in 12 CE and b) leachate solution in 121 CEC at 323 K (blue line) and 358 K (green line).



Figure S8: a) CV of 10 mM ferrocene in 121 CEC at RT for different scan rates. b) CV of 121 CEC at 298 K. WE: GC; CE: Pt; RE: Ag wire; Scan rate 20 mv/s.



Figure S9: a) CV of stacked view of leachate solution with different Ec at 358 K. WE: GC; CE: Pt; RE: Ag wire; Scan rate 20 mv/s. Each measurement represents an independent experiment using the same leachate solution, with the electrode cleaned between measurements. b) CV of the leachate solution (Ec = -1 V) showing two consecutive cycles at 358 K. (c) CV of the leachate solution with and without added water (0-6 wt.%) at 358 K. (d) CV of 0.1 M NiCl₂·6H₂O over three consecutive cycles at room temperature.

4. Preliminary studies on the choice of electrodes

Cu foam and SS were used as the WE and CE, and electrodeposition was performed for 30 min. Ni electrodeposition was observed on the Cu foam, further confirmed through SEM-EDX analysis, confirming the presence of pure Ni (Figure S10). On the other hand, the SS CE electrode exhibited discoloration, indicating corrosion that could not be removed using common organic solvents or water. This corrosion phenomenon can be attributed to the acidic nature of the leachate solution.

Subsequently, no electrodeposition was observed when the Cu foam was replaced with a planar Cu sheet as WE under the same electrodeposition conditions. Further attempts to increase the duration of the electrodeposition process did not result in successful deposition either. This is due to the unstable nature of both WE and CE, with WE being more pronounced in the case of the Cu sheet, likely due to its lower surface area than Cu foam. Additionally, further studies observed that the Cu sheet is not stable at 358 K.





Figure S10: SEM-EDX of Ni deposited on Cu foam (-0.7 V vs. Ag wire) at 358 K.



-0.7 V	Wt %
Ni	56.1
Cu	40.5
0	3.4





-0.8 V	Wt %
Ni	33.8
Cu	64.6
0	1.6





5 µm

Cu	04.0
0	1.6





-0.9 V	Wt %
Ni	38.2
Cu	59.2
0	2.6







Figure S11: SEM-EDX analysis of Ni deposition on a Cu sheet at 358 K for 30 minutes, with varied potential a) -0.7 V vs. Ag b) -0.8 V vs. Ag c) -0.9 V vs. Ag d) -1 V vs. Ag wire.



Cu Lα1,2

Ni Lα1,2



Figure S12: SEM-EDX of Ni deposited on Cu sheet at -1 V for 30 min at 358 K. a) Optical Image, b) SEM, c-e) EDX mapping of copper, nickel, and oxygen, respectively.

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Figure S13: SEM-EDX of Ni deposited on carbon paper at -1 V for 30 min at 358 K. a) Optical Image b) SEM c-e) EDX mapping of carbon, nickel, and oxygen, respectively.



Figure S14: SEM of Ni deposited on carbon paper at -1.4 V vs Ag wire for different temperatures and times.





Figure S16: Viscosity of 121 CEC and 181 CEC at different temperatures.



Figure S17: Leaching of Li and Ni from LNO using 181 CEC at 363 K.





Figure S18: SEM-EDX of Ni deposited on carbon paper from 181 CEC at -0.8 V for 30 min at 358 K. a) SEM b-e) EDX mapping of carbon, nickel, and oxygen, respectively.



Figure S19: a) SEM of commercial LNO and b) SEM/EDX of simulated black mass. The table shows the atomic percentages (At %) of elements detected in the simulated black mass.

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