APPLICATION NOTE

ICP-Optical Emission Spectroscopy

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Lithium-Ion Battery Recycling: Deep Eutectic Solvent Extraction of Cathode Active Materials with the Avio 220 Max ICP-OES

Introduction

The supply of raw materials is essential for every industrial chain and constitutes one of the bases of global growth. Rapid development of technology increases the demand for critical metals and minerals, which will double in the next 10 years.[1] In the European Union (EU), there is a strong imbalance between the demand for raw materials (RMs) and their supply, which is limited by the scarcity of mines. To guarantee secure access to these valuable products, the European Commission (EC) has established a list of "Critical Raw Materials".[1,2]

The demand for lithium-ion batteries (LIBs) is expected to grow exponentially in the near future, corresponding to a global battery production of ~500 GWh by 2025.[3-5] The essential RMs for LIBs are Co, Li, natural graphite (NG), Si, Ni and Mn, with Si, Co and NG considered scarce by the EC. The remaining elements (Li, Ni, Mn) are expected to become scarce in the next decades.

Metal demand in the battery industry can be supported by the transition to a circular economy through recycling and recovery of secondary raw materials via proper waste management.[1,2,6] To this end, the EU Battery Directive requires member States and industries to maximize the collection of spent batteries and to set up proper recycling treatments.[7]

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Spent LIBs are considered hazardous waste due to the presence of toxic oxides such as $LiCoO_2$, $LiMn_2O_4$, and $LiNiO_2$. Typical compositions of spent LIBs appear in Table 1. The current recovery methods for metal extraction (Co, Li, Ni) are pyrometallurgy and hydrometallurgy, which both consume large amounts of energy, require harsh conditions, and produce toxic waste materials.[8] As an alternative, soft solvometallurgy based on deep eutectic solvents (DESs) (a mixture of Lewis or Bronsted acids and bases which have unique properties) is gaining attention due to the combination of high recovery efficiency, low cost, biodegradability and, in some cases, the ability to dissolve metal oxides.[9]

Table 1. Typical Composition of Spent Lithium Batteries.[7]

Component	Composition
Co	5 - 20%
Ni	5 - 10%
Li	5 - 7%
Other Metals	5 - 10%
Organic Compounds	15%
Plastic	7%

In this work we take a first step in the use of deep eutectic solvents to extract critical metals (Li, Co, Ni, Mn) from pure cathode materials used in LIBs, focusing on $LiMn_2O_4$ (LMO), $LiNi_{0.8}Co_{0.2}O_2$ (LNCO) and $LiMn_{1.5}Ni_{0.5}O_4$ (LMNO). PerkinElmer's Avio® 220 Max hybrid simultaneous ICP-OES is used to measure the extracted metals in DES.

Experimental Conditions

Samples and Sample Preparation

The deep eutectic solvent (DES) was prepared as a 2:1 molar ratio mixture of choline chloride (ChCl) and lactic acid (Sigma-Aldrich, Milan, Italy). The mixture was heated at 50 °C while stirring until the ChCl completely dissolved in the lactic acid. Before use, the mixture was degassed for 15 minutes under N_2. Three different commercial cathode materials for Li-ion batteries cathode were investigated: $LiMn_2O_4$ (LMO), $LiNi_{0.8}Co_{0.2}O_2$ (LNCO) and $LiMn_{1.5}Ni_{0.5}O_4$ (LMNO) (Sigma-Aldrich, Milan, Italy).

Samples were prepared by dissolving 100 mg of the cathode material in 5 g of DES in an oil bath with continuous stirring. Oil bath temperatures from 20 - 170 °C were explored, while times varied from 5 - 24 hours. After heating and stirring, any undissolved residue was removed by filtration, followed by the addition of 10 mL of distilled water to the DES. For analysis, the sample was diluted 100x with 0.1% HNO_3 (v/v).

For LNCO, the metal-leaching procedure was optimized by means of an experimental design approach, where the leaching efficiency was determined by the following equation:

$$leaching\ (\%) = \frac{C_{M,f} \times V_s}{m_M} \qquad \text{(Eq. 1)}$$

where $C_{M,f}$ is the metal concentration in the leaching solution (mg/L), V_s is the initial leaching solution volume (L) and m_M is the amount of metal in the pristine cathode (mg).

Calibration Standards

Two series of different calibration standards were prepared in 2% HNO_3(v/v). The first series was prepared from a 10 ppm multielement calibration standard solution (Multi-Element Standard 3, PerkinElmer), with Li, Ni, and Mn concentrations of 0.6, 2.0, 5.0 and 10.0 mg/L. The second series of calibration standards was prepared from cobalt stock standard solution with Co concentrations of 1.0, 3.0, 6.0 and 10.0 mg/L. A linear calibration equation was used for all the elements.

Instrumentation

All the analyses were performed on the Avio 220 Max hybrid simultaneous ICP-OES, which features patented Flat Plate™ plasma technology[10] and a vertical torch design, providing a robust plasma for handling difficult matrices, such as organic solvents. The unique optical system[11,12] provides superior sensitivity and resolution for all elements of interest, as well as dual plasma view[13] and attenuation mode[14]. Combined, these features expand the dynamic range, allowing measurement of trace elements at extremely low concentrations in the same method as high-level elements. With patented Dynamic Wavelength Stabilization™, the Avio 220 Max can be completely powered down and restarted in 10 minutes, saving time, argon, and power consumption. In addition, the use of PlasmaShear™ technology[15] prevents carbon deposition on the interface when analyzing carbon-containing matrices (like DESs), which reduces maintenance while increasing signal stability.

The instrument operating parameters, analyte wavelengths, and plasma views are listed in Tables 2 and 3. Even though these samples contain 1% organic components (DES), standard sample introduction and plasma conditions are used, demonstrating the robustness of the Avio 220 Max system.

Table 2. Avio 220 Max ICP-OES Instrumental Parameters and Components.

Component / Parameter	Description / Value
Sample Uptake Rate	1.0 mL/min
Nebulizer	MEINHARD® Plus, K1
Spray Chamber	Baffled glass cyclonic
Spray Chamber Temperature	Room Temperature
Injector	Alumina, 2.0 mm i.d.
Torch	Quartz, 1-slot
Plasma Gas Flow	9 L/min
Auxiliary Gas Flow	0.2 L/min
Nebulizer Gas Flow	0.7 L/min
RF Power	1500 W

Table 3. Elements, Wavelengths, and Plasma Views.

Element	Wavelength (nm)	Plasma View
Co	228.616	Axial
Li	670.784	Radial
Mn	257.610	Radial
Ni	231.604	Radial

Results and Discussion

Spectral Information

One of the concerns when analyzing samples with elevated organic content is spectral interferences and noisy baselines caused by carbon emission lines. However, as shown in Figure 1, the baselines are flat, indicating the absence of carbon bands. The sensitivity of the Avio 220 Max system contributes to this in two ways: first, it allows samples to be diluted 100x which reduces the carbon content to 1%; and second, radial plasma view can be used for three of the four analytes. Radial plasma viewing reduces carbon spectral interferences (compared to axial view), since only a small cross-section of the plasma is being viewed. The results are excellent calibration curves, as shown in Figure 2.

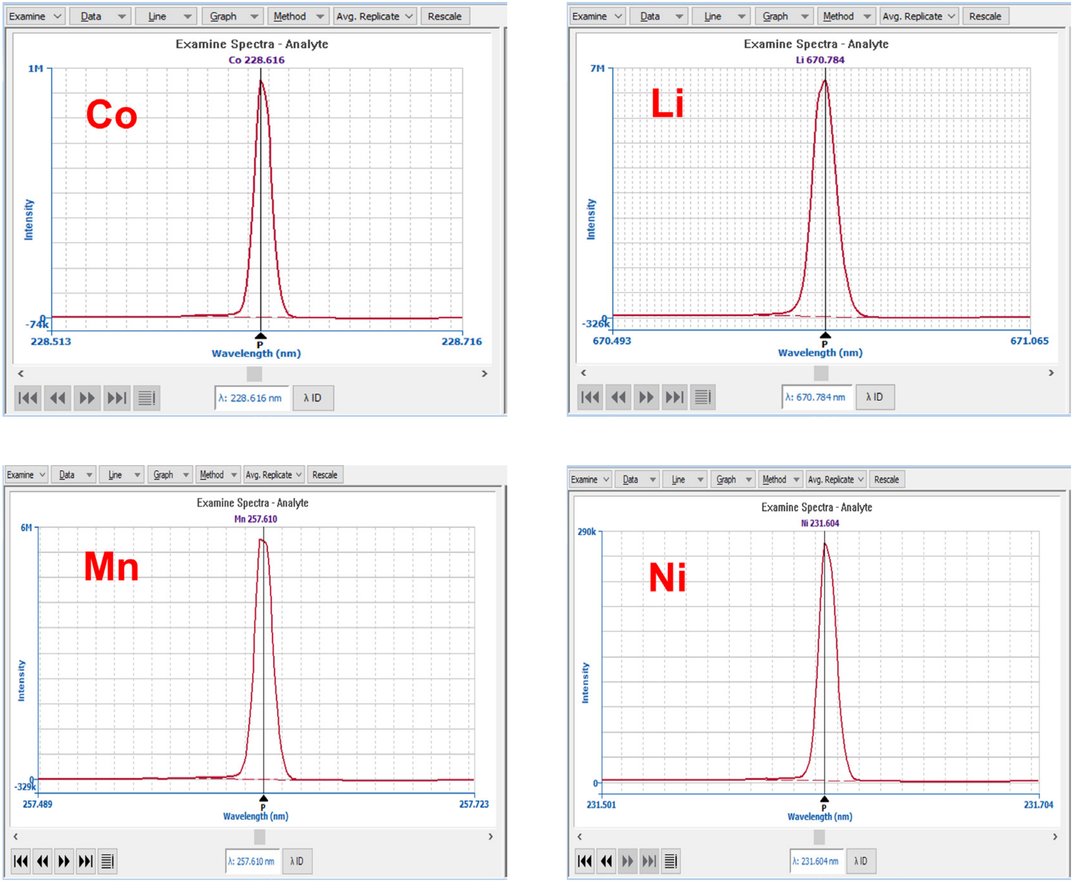

Figure 1. Spectra of 3 ppm Co, Li, Mn, and Ni in 1% DES, indicating the lack of carbon interferences.

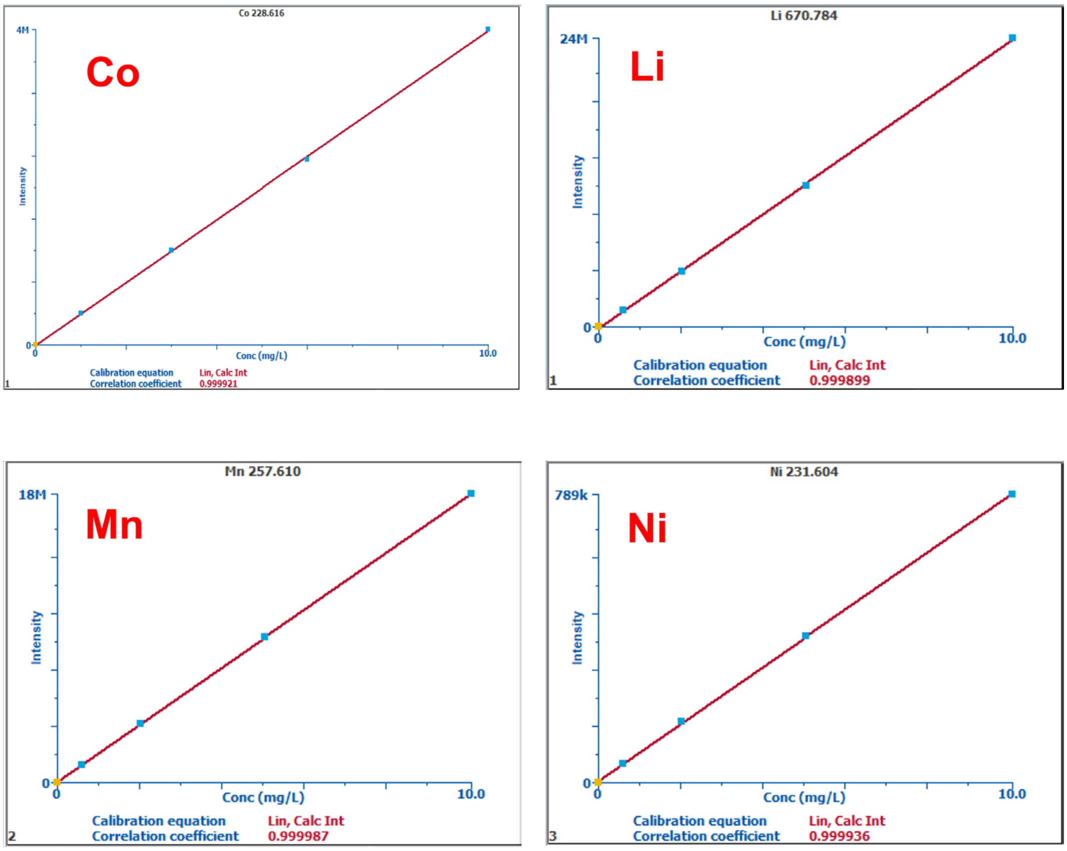

Figure 2. Calibration curves for Co, Li, Mn, and Ni.

$LiMn_2O_4$ (LMO) Leaching and Analysis

The DES leaching was first applied to $LiMn_2O_4$ to evaluate its effectiveness in extracting Li and Mn. Extraction temperatures (20, 70, 120, 170 °C) and times (5, 10, 15, 24 hours) were varied to determine which conditions provided the most efficient extraction. The results displayed in Figure 3a show that over half of Li and Mn can be extracted at 20 °C over 24 hours. By increasing the temperature to 70 °C, nearly all the Li and Mn are extracted.

Since 70 °C provides the highest extraction efficiency, this temperature was evaluated at different extraction times. As shown in Figure 3b, more than 90% of Li and Mn are extracted after 10 hours.

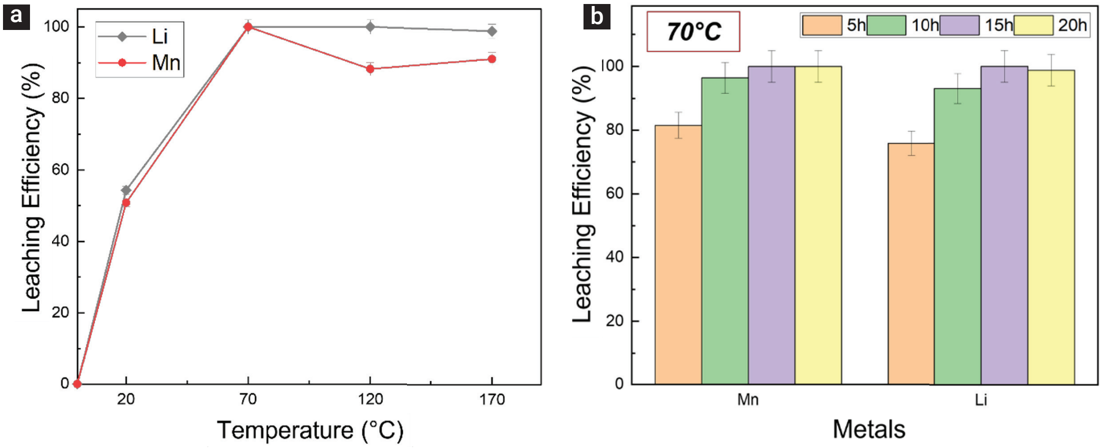

Figure 3. DES leaching efficiency of Li and Mn from $LiMn_2O_4$ (a) as a function of temperature over 24 hours; (b) as a function of leach time at 70 °C.

$LiMn_{1.5}Ni_{0.5}O_4$ (LMNO) Leaching and Analysis

The DES extraction efficiency was next evaluated for Li, Mn, and Ni in LMNO. As shown in Figure 4a, a 5-hour extraction at 100 °C was enough to recover nearly all the Mn (≈ 100%) and Ni (≈ 95%), but only ≈ 75% of the Li. Increasing the extraction time up to 20 hours (Figure 4b) did not significantly improve Li extraction. The low Li extraction efficiency is due to the partial precipitation of lithium salts, which were observed to settle out of solution over time (photo in Figure 4a).

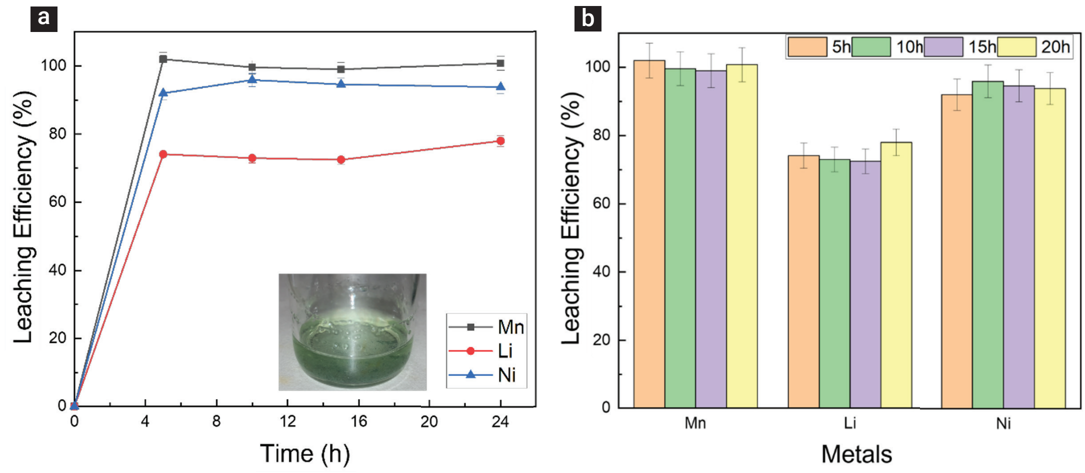

Figure 4. DES leaching efficiency of Li, Mn, and Ni from $LiMn_{1.5}Ni_{0.5}O_4$ as a function of time at 100 °C: (a) focus on time; (b) focus on metal. Formation of precipitate is shown in the inset photo in (a).

$LiNi_{0.8}Co_{0.2}O_2$ (LNCO) Leaching and Analysis

LNCO was evaluated for the extraction of Co using the optimized conditions for LMO and LMNO, but resulted in low Co recoveries (< 70%). Therefore, a more systematic approach using the Design of Experiments was carried out to determine the optimum extraction conditions for Li, Ni, and Co, with regards to temperature, time and quantity of DES. The limits of each variable were chosen so that the recovery process would be economically sustainable and favor industrial scalability. The ranges of each variable and resulting recoveries appear in Table 4, demonstrating that a temperature of 105 °C with 7.5 g of DES fully extracts Co, Li, and Mn within 5 hours.

Table 4. Leaching Efficiency of Co, Li, and Ni from LNCO Under Different Conditions.

Experiment	T (°C)	Time (h)	DES (g)	Leaching Efficiency (%)		
				Co	Li	Ni
1	50	5	2.5	33	41	31
2	105	5	2.5	88	72	87
3	50	24	2.5	52	59	51
4	105	24	2.5	88	74	88
5	50	5	7.5	62	62	62
6	**105**	**5**	**7.5**	**100**	**100**	**100**
7	50	24	7.5	71	68	71
8	105	24	7.5	100	100	100
9	77.5	14.5	5.0	65	67	65

Conclusion

This initial work demonstrates that PerkinElmer's Avio 220 Max ICP-OES provides simple and robust measurements in DES-based leachates of common cathode materials used in lithium-ion batteries, paving the way for extending this application to end-of-life lithium-ion batteries. The unique hybrid-simultaneous nature of the Avio 220 Max system permits the direct analysis of metal-containing DES solution which reduces reagents and increases throughput. The unique optical system and the dual plasma view result in excellent accuracy, reproducibility, and stability. The outstanding sensitivity, robustness, and ease-of-use of the Avio 220 Max ICP-OES make it well suited for quality control in LIBs recycling processes.

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Consumables Used

Component	Part Number
Multi-Element Solution 3, 10 ppm 125 mL	N9300233
Single-Element Standard: Cobalt, 1000 ppm	N9303766 (125 mL) N9300113 (500 mL)
MEINHARD® K1 LDV Nebulizer	N0811287
Quartz Torch, 1 slot	N0790131
2.0 mm i.d. Alumina Injector	N0791183
Sample Uptake Tubing: Black/Black (0.76 mm) i.d., PVC, Flared	N0777043
Drain Tubing: Red/Red (1.14 mm i.d.), PVC	09908585
Autosampler Tubes (500)	B0193233 (15 mL) B0193234 (54 mL)

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