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A novel method for screening deep eutectic solvent to recycle the cathode of Li-ion batteries

A classical electrochemical method was expanded to screen deep eutectic solvents (DESs) for recycling lithium-ion battery cathodes, and a choline chloride and urea DES was successfully employed to extract Li and Co, which was in good agreement with Fukui function calculation results.

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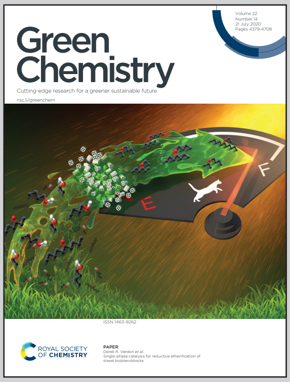

Volume 22
Number 14
21 July 2020
Pages 4379-4708

Green Chemistry

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rsc.li/greenchem

ISSN 1463-9262

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Cite this: *Green Chem.*, 2020, **22**, 4473

A novel method for screening deep eutectic solvent to recycle the cathode of Li-ion batteries†

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Received 27th February 2020,
Accepted 19th May 2020

DOI: 10.1039/d0gc00701c

rsc.li/greenchem

Deep eutectic solvents (DESs), as a green alternative technology, exhibit great potential to recycle valuable elements from spent lithium-ion batteries (LIBs). However, due to the weak reducing power of DESs, raising the temperature and extending the duration of processing are not efficient for screening suitable DESs for the recycling of LIBs. Here, we propose a novel, simple and robust experimental method to identify suitable DESs for recycling spent LIBs. Based on electrochemical principles, the method proposed in this study can be used to quickly determine the reducing power of DESs. As an example, a choline chloride (ChCl) and urea mixture as a DES was found to possess strong reducing power, with a Li and Co extraction efficiency of 95% from spent LIBs obtained at a reduced reaction temperature of 180 °C and reaction time of 12 h. The results are in good agreement with the results from Fukui functions calculations. The kinetic experiments revealed that the Li and Co extraction is controlled by solution and electron diffusion through the DES. Furthermore, a cubic cobalt oxide spinel (Co_3O_4) was obtained from the loaded DES using $H_2C_2O_4$ and NaOH in the dilution–precipitation–calcination process. The current strategy demonstrates great potential for rapid and reliable screening of suitable DESs for the effective recycling of spent LIBs.

Introduction

Rechargeable lithium-ion batteries (LIBs) have been widely utilized in fast-developing mobile devices, stationary storage devices and electric vehicles. Due to the large amounts of solid waste they produced, these batteries will be decommissioned in the next 3–6 years.[1–3] It is estimated that 30% of the vehicle market will comprise full battery electric vehicles, hybrid electric vehicles and plug-in hybrid electric vehicles by 2030.[4] The demands of LIBs will cause the approximate decuple production of the cathode materials.[4–6] Safe disposal of a large volume of spent LIBs is anticipated to be a major environmental challenge, and, at the same time, there is an anticipated shortage of raw materials that are used in LIBs. The establishment of effective LIB recycling strategies could balance the impact of end-of-life LIB waste and the demands on raw materials in the battery supply chain. The metal elements in the cathodes of spent LIBs are of huge socioeconomic value. For instance, the amount of cobalt and lithium present in LIB cathodes could be as high as 15 and 7 wt%,[7–11] respectively, contents much higher than those present in mined ores[1] and saline.[12] The recycling of these components from spent LIBs can maximize the use of metal elements, limit the risks of material shortages and reduce the dependency on supply chains while minimizing the impact of spent LIB waste on human health and the natural environment. However, the present technologies used to recycle spent LIBs still have many unresolved economic and environmental problems that limit their commercial applications.

At present, pyrometallurgy, hydrometallurgy or a combination of the two are typically used to recycle the metallic elements (*e.g.*, cobalt, lithium, nickel, copper, and manganese) in spent LIBs.[5,6,13–15] In the pyrometallurgy-dominant process, there are some inevitable disadvantages, such as high operating temperature (>1400 °C), high energy cost, harmful off-gas emissions, infrastructure scrubbing and less comprehensive metal recycling (Al and Li).[5,6,13] Although hydrometallurgy-dominant processes are preferred due to energy cost considerations, high purity and recovery rate of metals, hydrometallurgy-based processes suffer from high consumption of harmful chemicals (caustic mineral acid/alkaline solutions), long processing times (chemical reactions), expensive extractants, and secondary waste generation of waste acid, sludge and high salt solutions.[5,13,14] To reduce the adverse impact of the mineral lixiviants, organic acids and additives have also been investigated as substitutes for hazardous inorganic

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0gc00701c

acids.[9,16,17] However, the use of organic acids is still a huge challenge, due to their limited reducing and dissolving power, and poor thermostability.[1]

An exciting technology to recover valuable elements from spent LIBs is to use green solvents such as deep eutectic solvents (DESs) that provide suitable reducing and effective dissolving power for the desired elements.[1] The efficiency of extracting cobalt has been shown to be as high as 94.1% using a mixture (DES) of choline chloride and ethylene glycol (ChCl : EG), which approached the extraction efficiency of typical hydrometallurgical lixiviants.[1] With this DES, however, the reaction temperature and time were still high and long, at 220 °C and 24 h, which is not attractive for commercial operations.[1] Until now, an effective method to identify DESs that can effectively be used for the recycling of LIBs under mild processing conditions remains to be developed. The reducibility is known to control the dissolving power of DESs for Co(III) in the cathode of spent LIBs.[7] Thus, developing a novel method for analysing the reducibility of DESs is highly conducive to promoting applications of DESs in the reuse and recycling of spent LIBs.

In this study, we propose a novel, simple and rapid screening method involving DESs using electrochemistry-based cyclic voltammetry (CV) to determine the reducing power of DESs (shown in Scheme 1). Based on the results from Fukui functions calculations and CV analysis, a choline chloride and urea (ChCl : urea) mixture with strong reducibility could be considered to be a good DES candidate for extracting Li and Co from spent LIBs under mild conditions. To further understand the extraction mechanism, the apparent leaching kinetics were investigated and molecular structures of metal-loaded complexes were characterized. Finally, the cobalt in the loaded DES was recovered as spinel cobalt oxide (Co_3O_4) using a dilution–precipitation–calcination process. This study offers a novel insight into the analysis, design and optimization of DESs for use in the recycling of metals from spent LIBs.

Materials, methods and equations

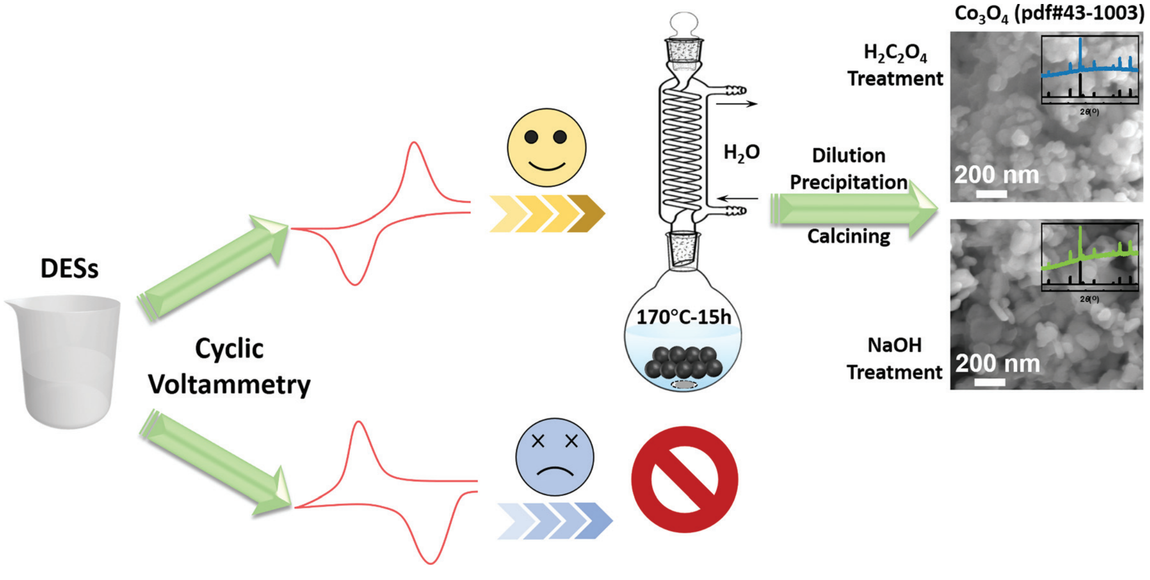
DES preparation and experiments

A clear, homogenous DES was formed by mixing choline chloride ($HOC_2H_4N[CH_3]_3Cl$; ≥98%; Macklin) with urea (CON_2H_4; ≥99%; Macklin) in a molar ratio of 1 : 2 at 80 °C for several hours.[18,19] $LiCoO_2$ (LCO) powder (≥97.87%; Aladdin) was used as a leaching raw material. All solutions were prepared using deionized water.

For metal extraction, LCO powder (0.1 g) and DES (5 g) were mixed in a glass flask. The glass flask with a condenser tube was placed in an oil bath. The effect of time and temperature on metal extraction was investigated over the time range of 1–24 h and temperature range of 140–180 °C at a speed of 125 rpm. The effect of the solid-to-liquid ratio was also assessed at 180 °C for 24 h. The leachates after the thermal experiment carried out at near to 100 °C were filtered using a filter membrane with a pore size of 0.45 μm.

Recovery experiments

The DES containing leached cobalt was recovered by precipitation in three solutions (saturated Na_2CO_3, saturated $H_2C_2O_4$, and 5 mol L^{-1} NaOH). Before the precipitation, the filtrate of the DES leachates (extracted at 1 g/25 g and 180 °C for 24 h) was diluted using deionized water and ethanol to 10 g of filtrate and 40 ml of diluent. The diluted filtrate was mixed with the equivalent volume of precipitant for 5 h and the mixture was then centrifuged at 12 000 rpm for 10 min. The precipitates were filtered using a membrane, where the filter cake was washed with deionized water until the filtrates remained clear



Scheme 1 The cyclic voltammetry (CV) method and recycling of spent lithium-ion batteries (LIBs).

upon the addition of $AgNO_3$ solution. The cleaned precipitate was then dried in a vacuum oven at 60 °C for 5 h and then calcined at 500 °C for 5 h.

Analysis of the DES and leachates

The metal cation concentration of the leachates was determined using inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 8000). The Fourier-transform infrared (FT-IR) and ultraviolet-visible (UV-Vis) spectra of the DES and leachates were obtained using a Nicolet iS50 FT-IR spectrometer in the form of KBr (potassium bromide) disks, and an Agilent Cary 60 UV-Vis spectrometer with a 1 mm-light path quartz cell. A three-electrode system with Pt as the working electrode (1 cm × 1 cm), Pt as the counter electrode and Ag as the reference electrode was used to acquire the CVs as a function of temperature from 140 to 180 °C using a CHI600E electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd, China). The electrodes were first washed with deionized water and ethanol using an ultrasonic cleaner for 10 min prior to their use.

Characterization of the calcined powders

The calcined powders were characterized by X-ray diffractometry (XRD, Rigaku SmartLab) using Cu Kα radiation, X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific), and field emission scanning electronic microscopy (FESEM, Zeiss Merlin).

Correlative equations in this study

The extraction efficiency, E, is calculated using eqn (1) as follows:

$$E = \frac{CV}{m_i} \times 100\% \tag{1}$$

Here, C is the metal cation concentration of leachate (mg L^{-1}), V is the initial leaching solution (L) and m is the initial mass (mg) of i element (Li or Co) in cathode material powders. The coefficient of the variation of the leaching efficiency was less than 5.0%.

The Fukui functions calculations from density functional theory (DFT) can be described by eqn (2) as follows:

$$\begin{aligned} f_A{}^+ &= q_A(N) - q_A(N+1), \quad \text{nucleophilic attack} \\ f_A{}^- &= q_A(N-1) - q_A(N), \quad \text{electrophilic attack} \\ f_A{}^0 &= (q_A(N-1) - q_A(N+1))/2, \quad \text{radical attack} \end{aligned} \tag{2}$$

where $q_A(N+1)$, $q_A(N)$, and $q_A(N-1)$ denote the charges at atom A on the anionic, neutral, and cationic species, respectively.

In the irreversible electrode reaction, the relationship between E_p or I_p and the scan rate can be described using eqn (3) and (4) as follows:[20,21]

$$E_p = E_{1/2} - \frac{RT}{\alpha nF}\left[0.780 + \ln\left(\frac{D^{0.5}}{k_s}\right) + \ln\left(\frac{\alpha nF}{RT}\right)^{0.5}\right] - \frac{RT}{\alpha nF}\ln \nu^{0.5} \tag{3}$$

$$I_p = 0.446nFAc^0\left(\frac{n\nu FD}{RT}\right)^{0.5} \tag{4}$$

Here, $E_{1/2}$ is the half-wave potential (V), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K), α is the electron transfer coefficient, n is the number of transferred electrons, F is Faraday's constant (96 500 C mol^{-1}), D is the electron diffusion coefficient, k_s is the heterogeneous electron transfer rate, c^0 is the solution concentration (mol L^{-1}), and ν is the scan rate (V s^{-1}).

The solution diffusion shrinking core model and Arrhenius equation can be described by eqn (5) and (6) as follows:

$$x = k \times t \tag{5}$$

$$\ln k = -\frac{E_a}{RT} + A \tag{6}$$

where x is the fraction of extracted metals, k is the leaching reaction rate constant (min^{-1}), E_a is the apparent activation energy, R is the universal gas constant (8.314 J K^{-1} mol^{-1}) and A is the frequency factor.

Results and discussion

Theoretical analysis of the DES in the recycling of metals from spent LIBs

In the process of metal electrodeposition, electropolishing, extraction and processing, DESs have been used due to their high solubility of metal oxides, such as NiO, MnO, Mn_2O_3, MnO_2, Co_3O_4, and CoO.[19,22–24] The cathodes of LIBs contain a number of polymetallic lithium oxides with high valence Co and/or Mn elements.[7] However, Co(III) and/or Mn(IV) oxides are usually insoluble. Reducing the valence of Co and/or Mn elements is therefore anticipated to play a key role in the recycling of these valuable elements from spent LIBs. In the recycling of spent LIBs using ChCl : EG DES, the oxidation of ethylene glycol is known to occur simultaneously with the reduction of Co from its +3 to +2 oxidation state.[1] However, the reducing power of ethylene glycol is rather limited, in that the extraction reactions occur at 220 °C for 24 h for the effective extraction of valuable elements from the spent LIBs. If the reduction potential of DESs could be made more negative, the corresponding reduction reaction and hence extraction of valuable elements from the spent LIBs could be accelerated. The redox reaction involves electron transfer between the elements. DFT calculations using Fukui functions (eqn (2)) have been used to determine whether elements act as electron donors (loss) or receptors (gain) in the electrochemical reactions of organic systems.[25–27] CV is on the other hand widely used to investigate the redox process of molecular species and electron transfer mechanisms.[20,28,29] The reducibility of DESs (reduction potential) can therefore be determined using Fukui functions calculations and verified using CV.

Urea is the simplest amide that contains both carbon and oxygen double bonds (C=O) and two amino groups (N–H). These groups can coordinate with metal ions to form metal–

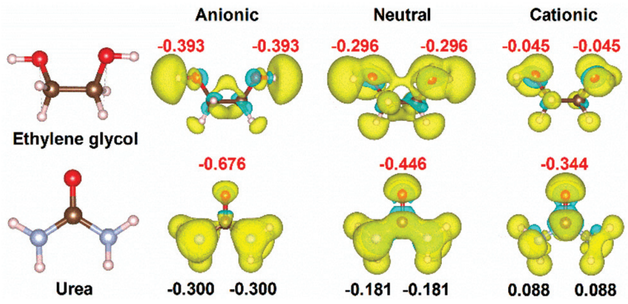


Fig. 1 Calculated f_A^-, f_A^0, and f_A^+ of O and N atoms in ethylene glycol and urea (the red values are for O and those in black are for N).

urea complexes *via* metal–O and metal–N bonds.[30] As a result, a ChCl : urea mixture could be considered as a good candidate for a DES.[18] In terms of ChCl : EG and ChCl : urea DESs, their reducing abilities arise from the hydrogen bond donor components, ethylene glycol and urea. To evaluate the reducibility of the two DESs, the atomic charges of ethylene glycol and urea were calculated using Fukui functions (Fig. 1). The f_A^+ values represent the reducibility of atoms according to their nucleophilic attack ability. The calculated order of f_A^+ values are the N atom in urea > the O atom in ethylene glycol > the O atom in urea. The highest reducibility of any atom was found to be the N in urea. This finding from Fukui functions calculations suggests that the reducibility of urea is higher than that of ethylene glycol. In order to further verify this result, the CVs of these two DESs were determined at a scan rate of 50 mV s^{-1}.

The CVs of the ChCl : EG and ChCl : urea DESs at temperatures between 140 and 180 °C are shown in Fig. 2A and B. Fig. 2A shows only one reduction peak in the CV of the ChCl : EG DES over the temperature range studied. The reduction current peak appeared from 0.40 to 0.50 V (*vs.* Ag). Fig. 2B also shows only one reduction current peak in the CV of the ChCl : urea DES over a temperature range of 140 to 180 °C. However, the reduction current peak in this case shifted significantly to between −0.45 and −0.35 V (*vs.* Ag). Although the reduction potential of the ChCl : urea DES became more positive upon an increase in the temperature from 140 to 180 °C, its reduction potential remains at around −0.35 V (*vs.* Ag), which is more negative than that of the ChCl : EG DES. This finding indicates that the reduction potential of the ChCl : urea DES is more negative than that of the ChCl : EG DES. Furthermore, the ionic activities of the DESs were found to increase with an increase in the temperature. The results from the CV study are consistent with the findings from the Fukui functions calculations. Based on the above study, the application of the ChCl : urea DES is anticipated to promote the reduction of Co(III) in the recycling of Co from the spent cathodes of LIBs.

The effect of the scan rate in the CV was determined from 10 to 150 mV s^{-1} from 160 to 170 °C (Fig. S1†). With an increase in the scan rate, the reduction peak potential (E_p) and current (I_p) shifted towards more negative values, indicating an irreversible electrode reduction reaction.[20,21] The relationships between E_p or I_p and ν (eqn (3) and (4)) are shown in Fig. 2C and D. The plots of E_p *vs.* $\ln((\nu/(\mathrm{V\ s^{-1}}))^{0.5})$ (Fig. 2C) and I_p *vs.* $(\nu/(\mathrm{V\ s^{-1}}))^{0.5}$ (Fig. 2D) show a good linear correlation with a correlation coefficient of above 0.990. The slopes of E_p *vs.* $\ln((\nu/(\mathrm{V\ s^{-1}}))^{0.5})$ at 160 and 170 °C are −0.119 and −0.080, respectively, which leads to the following relationships:

When $t = 160$ °C,

$$-\frac{RT}{\alpha nF} = -0.119, \quad \alpha n = 0.31$$

When $t = 170$ °C,

$$-\frac{RT}{\alpha nF} = -0.080, \quad \alpha n = 0.48$$

Since the number of transferred electrons for the ChCl : urea DES is constant, the above relationships show an

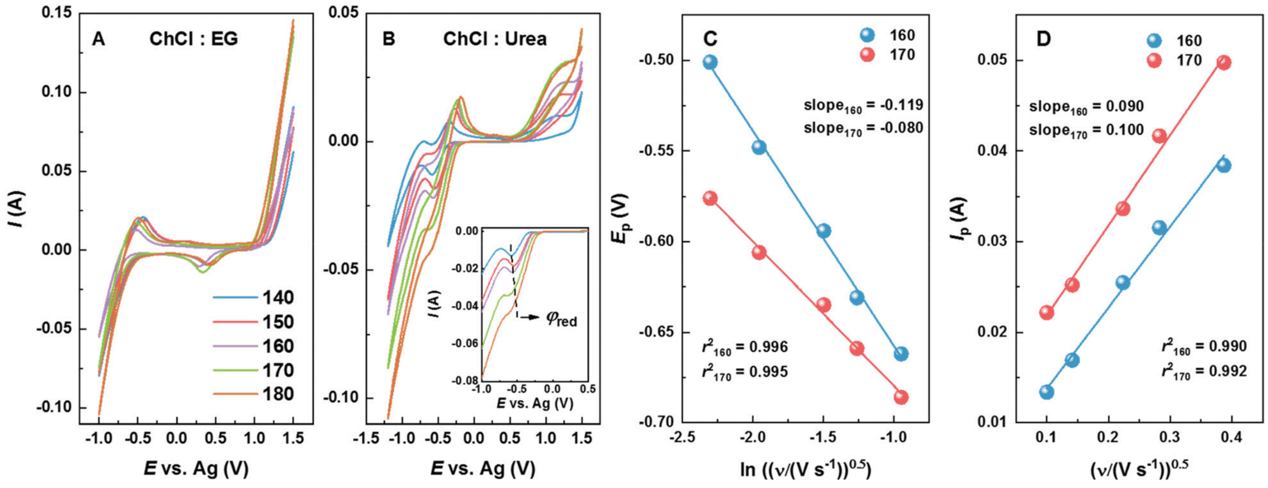


Fig. 2 Cyclic voltammograms of (A) ChCl : EG and (B) ChCl : urea DESs recorded at a fixed scan rate of 50 mV s^{-1} and the relationships of (C) E_p *vs.* $\ln((\nu/(\mathrm{V\ s^{-1}}))^{0.5})$ and (D) I_p *vs.* $(\nu/(\mathrm{V\ s^{-1}}))^{0.5}$.

increase in the electron transfer coefficient upon increasing the temperature. According to the Randles–Sevcik equation (eqn (4)),[20] a linear relationship of I_p *vs.* $(\nu)^{0.5}$ indicates a purely diffusion-controlled process. This finding suggests that the reduction reaction of the ChCl : urea DES is controlled by electron diffusion. An increase in temperature can increase the ionic activity, the reaction rates (increasing high energy collisions), electron transfer coefficient and electron diffusion (increasing molecular motion) of the ChCl : urea DES. An increase in temperature can therefore accelerate the reduction of the ChCl : urea DES.

In summary, it is theoretically and experimentally feasible to determine the reduction potential of DESs using CV. A more positive reduction potential of a DES is not beneficial for extracting metal cations from the LCO cathode. For the ChCl : EG DES with a reduction potential of 0.40–0.50 V (*vs.* Ag), the effective extraction of metal ions is achieved at 220 °C and 24 h.[1] According to Fukui function calculations and CV analysis, the stronger reducibility of the ChCl : urea DES with a more negative reduction potential of −0.45 to−0.35 V (*vs.* Ag) would lead to a more effective extraction of metal ions from the LCO cathode. In order to verify this prediction from the CVs, the effect of reaction temperature and time on the metal extraction from the LCO cathode was studied using the ChCl : urea DES.

Metal extraction

A range of mixtures of LCO powder (0.1 g) and the ChCl : urea DES (5 g) were allowed to react at a range of temperatures from 140 and 180 °C over a range of reaction times from 1 and 24 h. The concentrations of these Li- and Co-containing DESs were determined using ICP-OES (Fig. 3). From the determined concentrations of Li and Co in these DESs, the extraction efficiencies at the corresponding extraction times and temperatures were calculated. At 140 °C, the extraction efficiency of Li and Co from the LCO cathode increased slowly with increasing extraction time, but remained low at less than 12% for Li and 9% for Co up to an extraction time of 24 h (Fig. 3A and B). With an increase in the extraction temperature to 150 °C, the extraction efficiencies of Li and Co increased to 49% Li and 46% Co, respectively (Fig. 3A and B). At temperatures of above 150 °C, increasing the extraction time significantly increased Li and Co extraction. Over extraction temperatures of between 160 and 180 °C, there is a sharp increase in extraction efficiency from 1–6 h, followed by a gradual increase with a further increase in the extraction time up to 15 h, after which the extraction efficiency levelled off (Fig. 3A and B). An ultimate metal extraction efficiency of 80% was reached after 18 h at 160 °C and 90% after a shorter extraction time of 15 h at 170 and 180 °C (Fig. 3A and B). The extraction time and temperature had similar effects on the Li and Co concentrations in the DES as on their extraction efficiency, as anticipated (Fig. 3C and D). When Li and Co were extracted at 140 °C for 24 h, the DES contained only 0.2 g L^{-1} Li and 1.3 g L^{-1} Co. At 160 °C for 18 h, the Li and Co in the loaded DES increased to 1.5 and 12.8 g L^{-1}, respectively. The maximum values of Li and Co concentration were 1.7 and 14.4 g L^{-1}, respectively, reached at 180 °C after 18 h. These extraction efficiencies are as high as

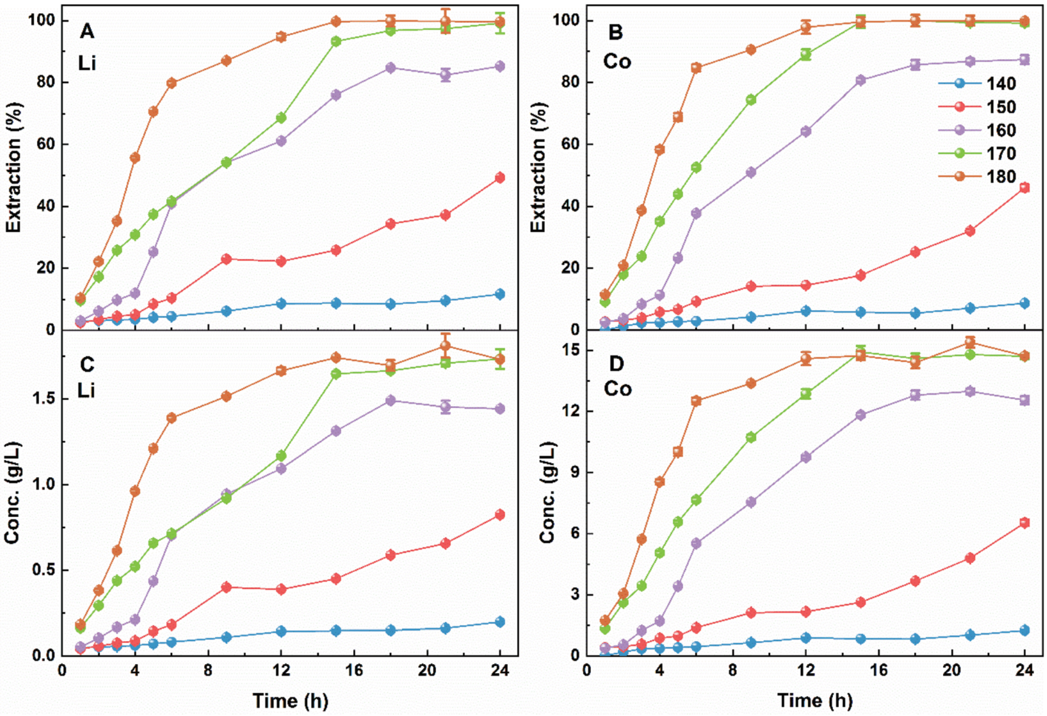


Fig. 3 Extraction of Li and Co using the ChCl : urea DES at various times and temperature in terms of the extraction of (A) Li and (B) Co, and concentration of (C) Li and (D) Co.

those achieved in hydrometallurgical processes using mineral acids,[31,34–36] organic acids[17,33,37] and ammoniacal solutions.[7,38–40]

Table 1 compares the results of metal extraction from LIB cathodes using DESs and hydrometallurgical processes. The Co extraction efficiencies of the ChCl : EG DES at 160, 180 and 220 °C for 24 h are 23.8%, 50.3% and 94.1%, respectively.[1] When the ChCl : urea DES was used as a lixiviant to extract metal from the LCO cathode, the extraction time could be shortened to 12 h to achieve Co extraction efficiencies of 64.2% at 160 °C, 89.1% at 170 °C and 97.9% at 180 °C. The results clearly show that a reduction in extraction temperature and time from 220 °C and 24 h to 180 °C and 12 h can be achieved by changing the DES from ChCl : EG to ChCl : urea. According to the theoretical analysis described earlier, the reduction of Co(III) plays a key role in enhancing Co extraction from the LCO cathode by the DES. The reduction potential of the ChCl : urea DES (−0.45 to −0.35 V (*vs.* Ag)) is more negative than that of the ChCl : EG DES (0.40–0.50 V (*vs.* Ag)), indicating the stronger reducibility of the ChCl : urea DES lixiviant than the ChCl : EG DES lixiviant under the same extraction conditions. Therefore, the extraction efficiency of Li and Co by the ChCl : urea DES is much higher than that of the ChCl : EG DES at the same extraction temperature but for only half the extraction time. Furthermore, the ionic activity, reaction rates, electron transfer coefficient and electron diffusion of the ChCl : urea DES were shown to increase with increasing extraction temperature. The extraction efficiency of Co increased from 6.3% to 97.9% upon an increase in the extraction temperature from 140–180 °C for 12 h. Although the Li and Co extraction efficiency in the hydrometallurgy process reached the same level of close to 100%, the hydrometallurgy process faces huge environmental pressure.[5,6,14] As green solvents, DESs have enormous potential in metal extraction, recycling and processing, with the development of rapid analysis techniques as described in this study.

In order to understand the dissolution mechanism of metals by DESs, the shrinking core model was used to fit the extraction kinetics data. As shown in Fig. S2,† the kinetic data fit well with the solution diffusion control model (eqn (5)). The good fit indicates that the solution diffusion on the surface of the unreacted core controls the leaching process of Li and Co from the LCO cathode by the DESs. This solution diffusion-controlled shrinking core model is different from that commonly used in the traditional hydrometallurgy processes that use acidic and ammoniacal solutions as the lixiviant (surface chemical reaction-controlled model).[7,38,41,42] Based on our theoretical analysis described above, the reduction reaction of the ChCl : urea DES is an electron diffusion-controlled irreversible reaction. Thus, increasing the temperature is anticipated to intensify the diffusion process of the solution and electrons. Furthermore, the ionic activity, reaction rates and electron transfer coefficient were shown to increase with an increase in the temperature of the reaction/extraction. These are the reasons for the significant increase in Li and Co extraction efficiency upon increasing the extraction temperature from 140 to 180 °C.

From the determined reaction rate constants and temperature, the apparent activation energy can be readily determined using the Arrhenius equation (eqn (6)). The apparent activation energies for extracting Li and Co were calculated to be 120.0 and 123.1 kJ mol^{-1}, respectively (Fig. S3†). These apparent activation energies are higher than those for extraction using acids (43.61 kJ mol^{-1} for Li, 41.52 kJ mol^{-1} for Co)[41] and ammoniacal solutions (83.30 kJ mol^{-1} for Li, 87.92 kJ mol^{-1} for Co).[42] These results provide scientific explanation for the changes in reaction conditions upon using various solutions to extract the valuable elements from spent LIBs, as shown in Table 1. The calculated apparent activation energy of metal extraction using various solutions is in the order of ChCl : urea DES > ammoniacal solutions > acids. Thus, the sequence of reaction temperature for metallic leaching from spent LIBs is ChCl : urea DES > ammoniacal solutions > acids.

In addition, the maximum load of Li and Co in the ChCl : urea DES was determined over a range of LCO masses (0.1–1.0 g) at 180 °C for 24 h (Fig. S4†). The Li and Co concentration in the DES increased upon increasing the LCO mass, but the Li and Co extraction efficiencies decreased as anticipated. At a solid-to-liquid mass ratio of 1.0 g/5 g equivalent to 240 g L^{-1}, which is much greater than that in hydrometallurgy

Table 1 Summary of the recycling of spent LIBs using DESs and hydrometallurgical processes

Extraction reagents	Samples	Conditions	Efficiency (%)
ChCl : EG DES[1]	LCO	160 °C, 24 h, 0.1 g/5 g (about 24 g L^{-1})	23.8 Co, 28.4 Li
		180 °C, 24 h, 0.1 g/5 g	50.3 Co, 89.8 Li
		195 °C, 24 h, 0.1 g/5 g	69.1 Co
		220 °C, 24 h, 0.1 g/5 g	94.1 Co
ChCl : urea DES	LCO	160 °C, 12 h, 0.1 g/5 g	64.2 Co, 61.2 Li
		170 °C, 12 h, 0.1 g/5 g	89.1 Co, 68.7 Li
		180 °C, 12 h, 0.1 g/5 g	97.9 Co, 94.7 Li
1 M HNO_3 + 1.7 vol% H_2O_2 [31]	LCO	75 °C, 1 h, 20 g L^{-1}	95 Co and Li
1 M H_2SO_4 + 10 g L^{-1} glucose[32]	LCO	80 °C, 4 h, 33.3 g L^{-1}	88 Co, 92 Li
2 M citric acid + 2 vol% H_2O_2 [33]	NCM[a]	80 °C, 1.5 h, 33.3 g L^{-1}	95 Co, 99 Li, 97 Ni, 94 Mn
6 M $NH_3·H_2O$ + 0.5 M $(NH_4)_2SO_3$ [7]	NCM	150 °C, 0.5 h, 10 g L^{-1}	100 Co, 98 Li, 74 Ni, 26 Mn

[a] NCM denotes $LiNi_xCo_yMn_zO_2$.

processes, the Li and Co extraction efficiencies decreased to 40.1% and 47.8%, respectively. In this case, the maximum values of Li and Co in the ChCl : urea DES are 7.5 and 77.5 g L^{-1}, respectively. It is evident that the Co present in the DES reached the concentration of cobalt-plating baths.[43,44]

The UV-Vis spectroscopic analysis of the DES containing Co(II) cations shows the signature bands under various conditions (Fig. 4A). A d–d broad band peak at 628 nm (λ) is present due to the formation of Co(II) complexes.[45] The absorbance of the broad peak is dependent on the concentration of the Co(II) cations in the DES. A linear relationship between the absorbance and Co concentration was found to be in good agreement with the Beer–Lambert law for this band. The broad band at 628 nm may be attributed to the typical electronic transition of ${}^4T_{1g}$ (F) → ${}^4T_{1g}$ (P) of an octahedral Co^{2+} cation.[46,47] That means that six coordinate covalent bonds exist in the Co(II) complexes. The ligands should be urea and Cl^-, with a central Co^{2+} cation. However, the formation of $[CoCl_3(urea)]^-$ with an absorption peak at 638 nm has been reported in a ChCl : urea DES containing 0.0589 g L^{-1} of $CoCl_2$.[48] When Co dissolves in the ChCl : urea DES from LCO, the Co concentration increases to 1.73 g L^{-1}, as shown in Fig. 4A. A tetrachlorocobaltate(II) ($[CoCl_4]^{2-}$) anions exist in the ChCl : EG DES.[1] According to the spectrochemical series, the splitting energy of urea is stronger than that of Cl^-. The Co^{2+} cation can coordinate with urea and Cl^- anions to be six-coordinated with octahedral geometry, where urea acts as a bidentate ligand. The urea molecule can bind with two Co^{2+} cations *via* its oxygen and nitrogen atoms. The six-coordinated complexes of Co^{2+} cations could be present in the form of $Co(urea)_2Cl_2$.

The FT-IR spectroscopy of the DES in the presence and absence of Co(II) were used to analyse the interactions between the various functional groups and identify structures using frequency shifts and absorption bands (Fig. 4B). The broad, strong bands at around 3347 and 3205 cm^{-1} are associated with the asymmetrical and symmetrical N–H stretching vibration bands of the amide group in urea, respectively.[21,48] The sharp, strong band at 1668 cm^{-1} is due to the C=O stretching vibration of the amide I band.[21,48] Furthermore, the sharp, strong band at 1622 cm^{-1} corresponds to the N–H bending vibration of the amide II band.[21,48] The sharp, medium band at 1450 cm^{-1} is associated with the C–N stretching vibration of the amide group.[21,48] The asymmetrical CCO stretching vibration band of ChCl occurs near to 956 cm^{-1}.[21,48] This means that the Ch^+ group is not changed in the ChCl : urea system. The FT-IR spectral comparison of the DES in the presence and absence of Co(II) is shown in Table S1.† When the DES contains Co(II), the absorption bands at 3347, 3205, 1668 and 1622 cm^{-1} become broader and stronger. This indicates that the amide group has reacted and changed in the Co-containing DES. A new absorption band occurs at 2208 cm^{-1} and its intensity becomes stronger with an increase in the Co concentration in the DES. This absorption band is associated with cobalt coordination compounds, in which the Co(II) cation coordinates with urea *via* a Co–O bond.[48] Furthermore, a satellite peak occurs at 2164 cm^{-1} in Co-containing DES at 180 °C after 2 and 4h, which may be due to the Co–N bond of cobalt coordination compounds.[30] This bond becomes weaker with increasing Co concentration. According to the UV-Vis analysis of the DES, the cobalt complexes may be in the form of $Co(urea)_2Cl_2$, with octahedral molecular geometry.

Based on Fukui functions calculations and CV analysis, the effect of the heating temperature and time on the metal extraction has been investigated according to the strength of the reducibility of the ChCl : urea DES. This ChCl : urea DES has been successfully used to recycle Li and Co from LCO under moderate conditions (180 °C for 12 h). This result is in accordance with the predictions of CV theoretical analysis. The metal extraction process is controlled by solution and electron diffusion, and its apparent activation energy is higher than

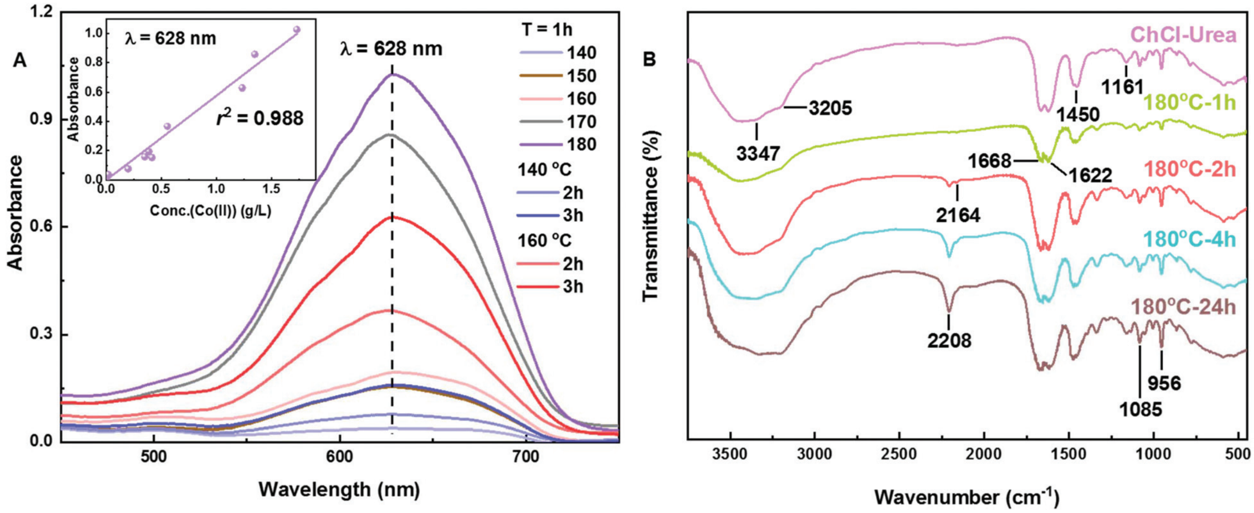


Fig. 4 (A) UV-Vis and (B) FT-IR spectra of the ChCl : urea DES and leachates at various extraction times and temperatures.

those of traditional hydrometallurgical methods. The maximum load of Li and Co by the DES reaches as high as those of hydrometallurgical methods. The structure of the ChCl : urea DES loaded with Co has been verified using UV-Vis and FT-IR spectra to contain octahedral complexes of Co (urea)$_2$Cl$_2$.

Metal recovery

The FESEM images, XRD patterns and XPS spectra of the recycled powder after calcination using three precipitants after ethanol dilution are shown in Fig. 5 and 6, respectively. The recycled powders were precipitated using $H_2C_2O_4$ (Fig. 5A and D), Na_2CO_3 (Fig. 5B and E), and NaOH (Fig. 5C and F) solutions. The particle sizes of the three calcined powders is less than 300 nm, where the particle size trend using various precipitants is in the order of NaOH > $H_2C_2O_4$ > Na_2CO_3. The shapes of the calcined powder particles are also different, such as the irregular balls or sheets observed for $H_2C_2O_4$, irregular sheets for NaOH, and balls for Na_2CO_3. However, the recycled powders diluted with deionized water were precipitated using $H_2C_2O_4$ (Fig. S5A and S5D†), Na_2CO_3 (Fig. S5B and S5E†), and NaOH (Fig. S5C and S5F†) solutions. The particle sizes of these calcined powders are also less than 300 nm and they show a similar trend in particle size to that described above, where these particle sizes are a little larger than those shown in Fig. 5. Furthermore, their shapes are similar to those observed after ethanol dilution. The effect that the diluting solvent had on the appearance of the recycled powders was negligible.

In the XRD patterns, the peaks of the crystalline recycled powders diluted with ethanol (Fig. 6A) and deionized water

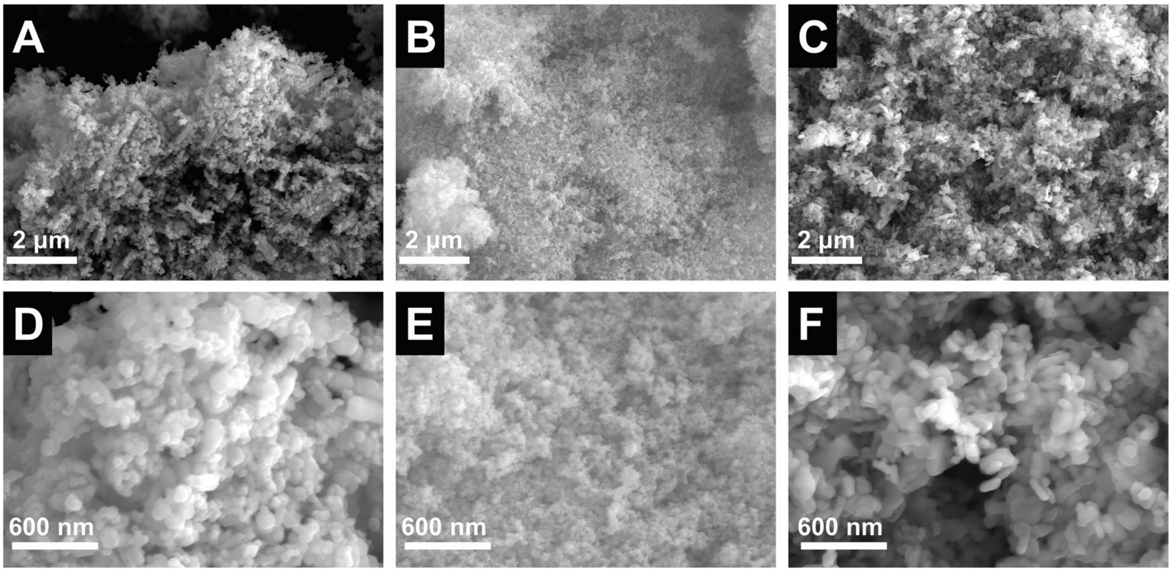


Fig. 5 FESEM images of the calcined powder after ethanol dilution using $H_2C_2O_4$ (A and D), Na_2CO_3 (B and E) and NaOH (C and F).

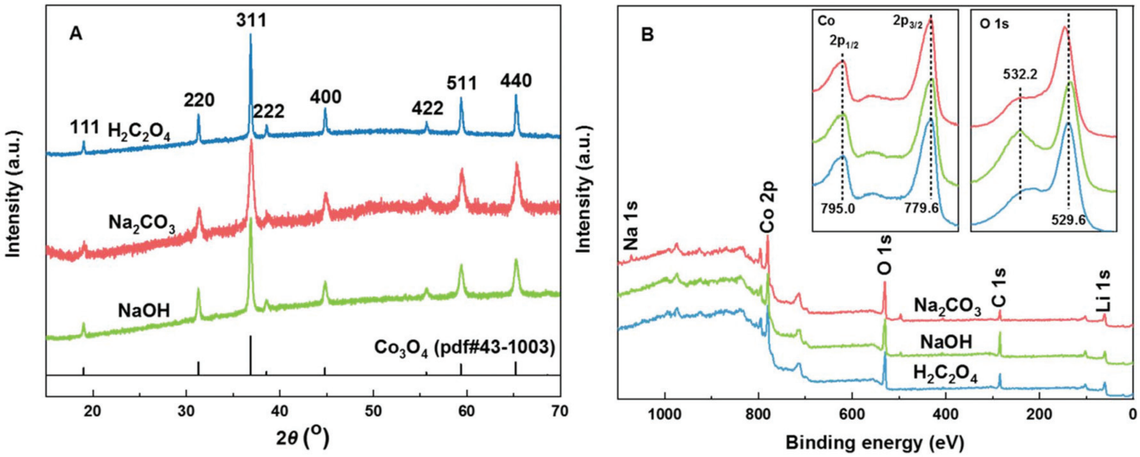


Fig. 6 (A) XRD patterns and (B) XPS spectra of the calcined powder after ethanol dilution.

(Fig. S6†) can be well matched to cubic cobalt oxide spinel (XRD standard card: JCPDS no. 43-1003). A cubic cobalt oxide spinel can be also obtained using Na_2CO_3 solution and loaded ChCl : EG DES.[1] However, the crystallinity of the recycled powders diluted with ethanol is better than that of those diluted with deionized water. The crystallinity according to the use of different precipitants *via* ethanol dilution is $H_2C_2O_4 > NaOH > Na_2CO_3$. The effect of the precipitants on the crystallinity of the recycled powders *via* dilution using deionized water was ignored, as their crystallinity was not good.

XPS spectroscopy is used to analyse the chemical composition and valence state of materials, so the recycled powders after ethanol dilution (Fig. 6B) and deionized water dilution (Fig. S7†) were determined by XPS. In the survey scan spectra (Fig. 6B and S7†), the Co, C, O, and Li elements were found in all of the calcined powders, and the additional element Na was found to be present in the calcined powder precipitated using Na_2CO_3. That means that the Na element in the calcined powder precipitated using Na_2CO_3 is not removed from the powder by the deionized water. The Co 2p spectrum peaks of the calcined powder after ethanol dilution are shown at 779.6 eV (narrow, strong) and 795.0 eV (medium), which could be due to Co $2p_{1/2}$ (a medium peak) and Co $2p_{3/2}$ (a narrow, strong peak) in Li_xCoO_2.[49,50] Meanwhile, a narrow, strong O 1s peak near to 529.6 eV with a satellite peak near to 532.2 eV are observed in the calcined powder after ethanol dilution.[49,50] These peaks are most probably due to O^{2-} anions from Li_xCoO_2 in the subsurface. However, the O 1s peak of the calcined powder precipitated using Na_2CO_3 is slightly shifted to the left. Although this shifted peak also represents O^{2-} anions, they may be different oxides, such as the oxygen in the carbonate anion. Similar XPS results for the Co 2p and O 1s spectra peaks were observed for the recycled powders after dilution in deionized water.

The most Co in the ChCl : urea DES was recycled in the process of dilution–precipitation–calcination to be cubic cobalt oxide spinel (Co_3O_4), containing some Li. According to the XRD and XPS results, the preferred precipitants were$H_2C_2O_4$ and NaOH rather than Na_2CO_3 under calcining conditions of 500 °C for 5 h. The results of the precipitants $H_2C_2O_4$ and NaOH were different to those described in previous reports[1] in two ways: (1) the crystallinity of the calcined powder precipitated using Na_2CO_3 was worse than the others and (2) the Na in the hydrated cobaltous carbonate was difficult to remove.

Conclusions

The lithium polyoxometalates in spent LIBs have been dissolved into DESs. The high valence of the Co cation plays an adverse role in the recycling of valuable components from spent LIBs. Here, we demonstrate that by using DESs with a more negative reduction potential, the temperature and reaction duration can be significantly reduced. The main conclusions of this work are as follows:

(1) CV is a rapid and effective electrochemical method that can be used to analyse the reducibility of DESs. The reduction potential of the ChCl : urea DES is more negative than that of the ChCl : EG DES. We found that the ChCl : urea DES is very effective in recycling Li and Co from spent LIBs, which is in good agreement with the results of the Fukui functions calculations. Raising the temperature greatly accelerates the reduction reaction.

(2) The Li and Co extraction efficiency was around 95% at a temperature of 170/180 °C and duration of 12 h. The optimal amounts of Li and Co in the ChCl : urea DES were found to be 7.5 and 77.5 g L^{-1}, respectively. Solution and electron diffusion processes were found to control the recycling process on the basis of mathematical fitting results.

(3) The structure of the Co complexes in the ChCl : urea DES was verified from UV-Vis and FT-IR spectral analysis to be octahedral $Co(urea)_2Cl_2$.

(4) The Co can be recycled as a cubic cobalt oxide spinel (Co_3O_4) using $H_2C_2O_4$ and NaOH precipitants using a dilution-precipitation–calcination process.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was financially supported by the National Natural Science Foundation of China (51772141). This work was also supported financially by the Shenzhen Science and Technology Innovation Committee (KQJSCX2018032215150778, JCYJ20170817111443306) and the Shenzhen Peacock Plan (KQTD20160226195840229). Additional support was provided by the Guangdong Province Universities and Colleges Pearl River Scholar Funded Scheme 2018.

Notes and references

1 M. K. Tran, M. T. F. Rodrigues, K. Kato, G. Babu and P. M. Ajayan, *Nat. Energy*, 2019, **4**, 339–345.
2 X. Zheng, Z. Zhu, X. Lin, Y. Zhang, Y. He, H. Cao and Z. Sun, *Engineering*, 2018, **4**, 361–370.
3 X. Chen, D. Kang, L. Cao, J. Li, T. Zhou, H. J. S. Ma and P. Technology, *Sep. Purif. Technol.*, 2019, **210**, 690–697.
4 Global EV Outlook 2019, https://webstore.iea.org/global-ev-outlook-2019, (accessed 18, December, 2019).
5 X. Zhang, L. Li, E. Fan, Q. Xue, Y. Bian, F. Wu and R. Chen, *Chem. Soc. Rev.*, 2018, **47**, 7239–7302.
6 E. Fan, L. Li, Z. Wang, J. Lin, Y. Huang, Y. Yao, R. Chen and F. Wu, *Chem. Rev.*, 2020, DOI: 10.1021/acs.chemrev.9b00535.
7 S. Wang, C. Wang, F. Lai, F. Yan and Z. Zhang, *Waste Manage.*, 2020, **102**, 122–130.

8 J. Li, X. Li, Q. Hu, Z. Wang, J. Zheng, L. Wu and L. Zhang, *Hydrometallurgy*, 2009, **99**, 7–12.

9 X. Zhang, H. Cao, Y. Xie, P. Ning, H. An, H. You and F. Nawaz, *Sep. Purif. Technol.*, 2015, **150**, 186–195.

10 X. Chen, J. Li, D. Kang, T. Zhou and H. Ma, *Green Chem.*, 2019, **21**(23), 6342–6352.

11 X. Chen, D. Kang, J. Li, T. Zhou and H. Ma, *J. Hazard. Mater.*, 2020, **389**, 121887.

12 G. Liu, Z. Zhao and A. Ghahreman, *Hydrometallurgy*, 2019, **187**, 81–100.

13 C. Liu, J. Lin, H. Cao, Y. Zhang and Z. Sun, *J. Cleaner Prod.*, 2019, **228**, 801–813.

14 G. Harper, P. Slater, R. Sommerville, R. Stolkin, S. Lambert, A. Abbott, E. Kendrick, A. Walton, K. Ryder, L. Driscoll, L. Gaines, P. Christensen, O. Heidrich and P. Anderson, *Nature*, 2019, **575**, 75–86.

15 R. E. Ciez and J. F. Whitacre, *Nat. Sustainability*, 2019, **2**, 148–156.

16 L. Li, J. Ge, F. Wu, R. Chen, S. Chen and B. Wu, *J. Hazard. Mater.*, 2010, **176**, 288–293.

17 C. S. dos Santos, J. C. Alves, S. P. da Silva, L. E. Sita, P. R. C. da Silva, L. C. de Almeida and J. Scarminio, *J. Hazard. Mater.*, 2019, **362**, 458–466.

18 A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, *Chem. Commun.*, 2003, 70–71.

19 E. L. Smith, A. P. Abbott and K. S. Ryder, *Chem. Rev.*, 2014, **114**, 11060–11082.

20 N. Elgrishi, K. J. Rountree, B. D. McCarthy, E. S. Rountree, T. T. Eisenhart and J. L. Dempsey, *J. Chem. Educ.*, 2017, **95**, 197–206.

21 D. Y. Yue, Y. Z. Jia, Y. Yao, J. H. Sun and Y. Jing, *Electrochim. Acta*, 2012, **65**, 30–36.

22 A. P. Abbott, G. Capper, D. L. Davies, K. J. Mckenzie and S. U. Obi, *J. Chem. Eng. Data*, 2006, **51**, 1280–1282.

23 F.-J. Albler, K. Bica, M. R. S. Foreman, S. Holgersson and M. S. Tyumentsev, *J. Cleaner Prod.*, 2017, **167**, 806–814.

24 D. Di Marino, M. Shalaby, S. Kriescher and M. Wessling, *Electrochem. Commun.*, 2018, **90**, 101–105.

25 F. De Proft, C. Van Alsenoy, A. Peeters, W. Langenaeker and P. Geerlings, *J. Comput. Chem.*, 2002, **23**, 1198–1209.

26 W. Tiznado, E. Chamorro, R. Contreras and P. Fuentealba, *J. Phys. Chem. A*, 2005, **109**, 3220–3224.

27 P. Fuentealba, E. Florez and W. Tiznado, *J. Chem. Theory Comput.*, 2010, **6**(5), 1470–1478.

28 A. Abbott, G. Frisch, S. Gurman, A. Hillman, J. Hartley, F. Holyoak and K. Ryder, *Chem. Commun.*, 2011, **47**, 10031–10033.

29 C. A. Nkuku and R. J. Lesuer, *J. Phys. Chem. B*, 2007, **111**, 13271.

30 T. Theophanides and P. D. Harvey, *Coord. Chem. Rev.*, 1987, **76**, 237–264.

31 C. K. Lee and K.-I. Rhee, *Hydrometallurgy*, 2003, **68**, 5–10.

32 F. Pagnanelli, E. Moscardini, G. Granata, S. Cerbelli, L. Agosta, A. Fieramosca and L. Toro, *J. Ind. Eng. Chem.*, 2014, **20**, 3201–3207.

33 X. Chen and T. Zhou, *Waste Manage. Res.*, 2014, **32**, 1083–1093.

34 L.-P. He, S.-Y. Sun, X.-F. Song and J.-G. Yu, *Waste Manage.*, 2017, **64**, 171–181.

35 W. Lv, Z. Wang, H. Cao, X. Zheng, W. Jin, Y. Zhang and Z. Sun, *Waste Manage.*, 2018, **79**, 545–553.

36 K. Tanong, L. Coudert, M. Chartier, G. Mercier and J. F. Blais, *Environ. Technol.*, 2017, **38**, 3167–3179.

37 X. Zeng, J. Li and B. Shen, *J. Hazard. Mater.*, 2015, **295**, 112–118.

38 C. Wu, B. Li, C. Yuan, S. Ni and L. Li, *Waste Manage.*, 2019, **93**, 153–161.

39 K. Meng, Y. Cao, B. Zhang, X. Ou, D.-m. Li, J.-f. Zhang and X. Ji, *ACS Sustainable Chem. Eng.*, 2019, **7**, 7750–7759.

40 H. Ku, Y. Jung, M. Jo, S. Park, S. Kim, D. Yang, K. Rhee, E.-M. An, J. Sohn and K. Kwon, *J. Hazard. Mater.*, 2016, **313**, 138–146.

41 W. Gao, X. Zhang, X. Zheng, X. Lin, H. Cao, Y. Zhang and Z. Sun, *Environ. Sci. Technol.*, 2017, **51**, 1662–1669.

42 X. Zheng, W. Gao, X. Zhang, M. He, X. Lin, H. Cao, Y. Zhang and Z. Sun, *Waste Manage.*, 2017, **60**, 680–688.

43 M. I. Jeffrey, W. Choo and P. Breuer, *Miner. Eng.*, 2000, **13**, 1231–1241.

44 A. E. Elsherief, *J. Appl. Electrochem.*, 2003, **33**, 43–49.

45 K. Sawada and T. Suzuki, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2301–2306.

46 M. Sönmez, A. Levent and M. Şekerci, *Synth. React. Inorg. Met.-Org. Chem.*, 2003, **33**, 1747–1761.

47 M. Sönmez, İ. Berber and E. Akbaş, *Eur. J. Med. Chem.*, 2006, **41**, 101–105.

48 X. Z. Cao, L. L. Xu, Y. Y. Shi, Y. W. Wang and X. X. Xue, *Electrochim. Acta*, 2019, **295**, 550–557.

49 L. Dahéron, R. Dedryvère, H. Martinez, M. Ménétrier, C. Denage, C. Delmas and D. Gonbeau, *Chem. Mater.*, 2007, **20**, 583–590.

50 L. A. Montoro, M. Abbate and J. M. Rosolen, *Electrochem. Solid-State Lett.*, 2000, **3**(9), 410–412.