RSC Sustainability

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal

Cite this: DOI: 10.1039/d5su00737b

Received 9th September 2025
Accepted 3rd October 2025

DOI: 10.1039/d5su00737b

rsc.li/rscsus

Metal recovery from 'black mass' of spent alkaline batteries using aqueous protic ionic liquids and deep eutectic solvents

Spyridon Koutsoukos, Chang Liu, Krishna V. Kinhal, Tongxin Liu, Francis P. Roche and Francisco Malaret *

Black mass, the crushed electroactive residue of the battery recycling process, is a valuable secondary source of critical metals. In this work, we present a two-step process, employing deep eutectic solvents and protic ionic liquids for low-temperature fractionalisation of black mass. This method achieved selective recovery of Zn and Mn, demonstrating a more sustainable and efficient alternative to conventional metal separation techniques.

Sustainability spotlight

The depletion of primary sources for critical materials like zinc and manganese, essential for battery production, underscores the urgent need for the development of efficient and sustainable battery recycling technologies. This work explores the use of protic ionic liquids and deep eutectic solvents in the selective extraction of those metals from the black mass of spent alkaline batteries. By enabling efficient separation and valorisation of critical materials, the process takes us one step closer to reducing environmental impact and supporting resource circularity. This work directly contributes to SDG 12 (Responsible consumption and production) and SDG 9 (Industry, Innovation and Infrastructure).

Introduction

Black mass (BM) is the metal-rich powder generated during battery recycling, which contains a mixture of metals derived from the anodes and cathodes, in addition to electrolyte residue. BM accounts for approximately 40–50% of total battery weight and, depending on its source, is rich in metals like Zn, Fe, Ni, Co, Cu, and Mn, usually in the forms of alloys or oxides.[1,2] Recovering metals from BM is of utmost importance for two main reasons: (1) BM can be a significant source of valuable materials, as most of the metals mentioned above are characterised as 'rare' or 'critical' by the European Union and the European Chemical Society[3] and (2) due to the significant presence of heavy and transition metals, which can penetrate groundwater, BM is considered highly toxic (CMR risk) and cannot be disposed of in landfills without further treatment.[4]

The most common methods for metal recovery from BM are pyrometallurgy and hydrometallurgy. In a typical pyrometallurgical process, BM is heated to high temperatures (1500–2500 °C), together with a reducing agent (*e.g.* CO) which converts metal oxides to their pure metal form, before the molten metals are separated from the floating unmelted components.[5,6] The pyrometallurgical approach, although allowing for high recovery rates and purities, suffers from high energy requirements and the emission of significant quantities of CO_2 and other hazardous gases (as by-products of the incineration of residual organic compounds/polymeric binders). On the other hand, hydrometallurgical approaches benefit from much lower operational temperatures (typically 50 to 200 °C) and reduced emissions,[7] making them more environmentally sustainable alternatives. However, hydrometallurgical processes suffer from a lack of selectivity and a dependence on consecutive solvent extraction steps, adding to both the cost and complexity.[8]

Ionic liquids and deep eutectic solvents have emerged as promising solvents for the extraction and separation of metals from BM.[9] Their negligible volatility, high thermal stability and wide electrochemical windows,[10] combined with their ability to dissolve and coordinate metal ions,[11] make them excellent candidates for the treatment of polymetallic waste and the valorisation of metals.[12] The majority of published work focuses on the use of hydrophobic ionic liquids as solvents for liquid–liquid extraction of acidic BM leachates,[13–15] although these systems have been less well explored for the direct leaching of targeted metals from the BM dust.[16,17]

While progress in this space has been promising, ionic liquids (especially aprotic) are expensive, often the result of energy-intensive, multi-step synthesis procedures, and their use as solvents on an industrial scale typically renders the process economically non-viable.[18] Nevertheless, the vast chemical diversity of ionic liquids posits the existence of specific subclasses capable of overcoming these limitations.[19] In order for this technology to reach commercialisation, it is crucial to explore ways to reduce ionic liquid-associated costs. Working

Nanomox Ltd, 21 Albemarle St., London, UK. E-mail: f.malaret@nanomox.net

towards this, we have explored deep eutectic solvents and aqueous protic ionic liquids (Fig. 1) as solvents for the extraction of target metals from BM. Both of these solvent types have significantly reduced production costs compared to aprotic ionic liquids, since their synthesis involves an easily scalable one-step component mixing under heating[20] or neutralisation of a Brønsted acid and base accordingly.[21]

In this study, we investigated the use of aqueous protic ionic liquids and deep eutectic solvents for the selective extraction of Zn and Mn from BM derived from spent alkaline batteries. Through systematic screening of solvent systems, we identified combinations that enable targeted leaching of Zn under mild conditions. We have created an efficient two-step process which generates two leachates, one rich in Zn (over 85% Zn purity) and one rich in Mn (over 70% Mn purity) and a combined yield of 100% Zn leaching and 79% Mn leaching from the BM.

Results and discussion

The composition of BM can vary significantly depending on battery type. This study focussed on BM from alkaline batteries as it represents up to 72% of battery waste collected in the EU,[22] and was provided by Ever Resource Ltd. BM is a heterogeneous material; to overcome this, the BM was pre-treated by drying, crushing and sieving in order to remove extremely small and large particles (see the SI for detailed sample preparation). The processed BM samples had a particle size distribution between 300 nm and 1800 nm, with a maximum moisture content of 3% w/w. The BM was initially characterised *via* X-ray fluorescence (XRF) spectroscopy and X-ray diffraction, in order to identify the major components, which were MnO, ZnO and zinc ferrites (see Fig. S4). Accurate determination of the mass percentage was performed *via* Inductively Coupled Plasma Mass Spectrometry (ICP-MS), which revealed a % w/w composition of: Mn: 33.1 ± 1.1%, Fe: 2.8 ± 0.4%, Zn: 25.0 ± 0.4%. Detailed experimental procedures are provided in the SI.

Control extractions with H_2O, H_2SO_4 and NaOH

One of the benefits of using ionic liquids and deep eutectic solvents as reaction or extraction solvents is that altering their constituents allows for tailoring of a wide range of physico-chemical properties, such as polarity, hydrophobicity, acidity/basicity, ionicity *etc.*[23,24] In this work, we focussed on polar, hydrophilic and water-miscible systems, aiming to use water as the extraction co-solvent. Acidity of the solvent is an important extraction parameter, which is difficult to determine from first principles. Therefore, preliminary extraction experiments were performed in H_2O, 1 M H_2SO_4 and 1 M NaOH, in order to understand the leaching behaviour of BM under neutral, acidic and basic conditions (Fig. 2). We tested three time points (2, 4 and 24 h) and two temperatures (30 °C and 80 °C), while the solid-to-liquid ratio was kept constant at 1 g/30 mL. The results demonstrated that the material had low solubility in water, with 8–10% maximum BM dissolution depending on the process parameters; ICP-MS results demonstrated no significant loss of the metals of interest (*i.e.* Mn, Zn, Fe), indicating that the soluble fraction is attributed to soluble salts (*e.g.* KOH residuals of the battery electrolyte) or residual organic matter. When 1 M H_2SO_4 was used as the extraction solvent, the BM dissolution

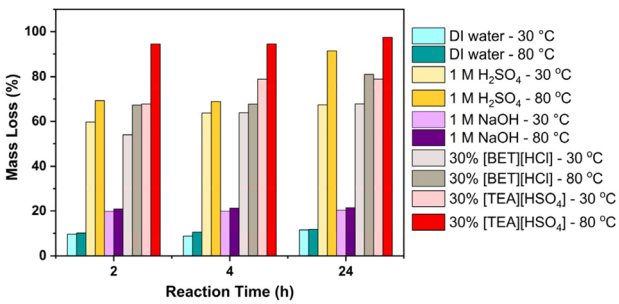

Fig. 2 Mass loss after treatment of BM with DI water, 1 M H_2SO_4, 1 M NaOH, 30% [Bet][HCl] and 30% [TEA][HSO_4] at 2 h, 4 h and 24 h.

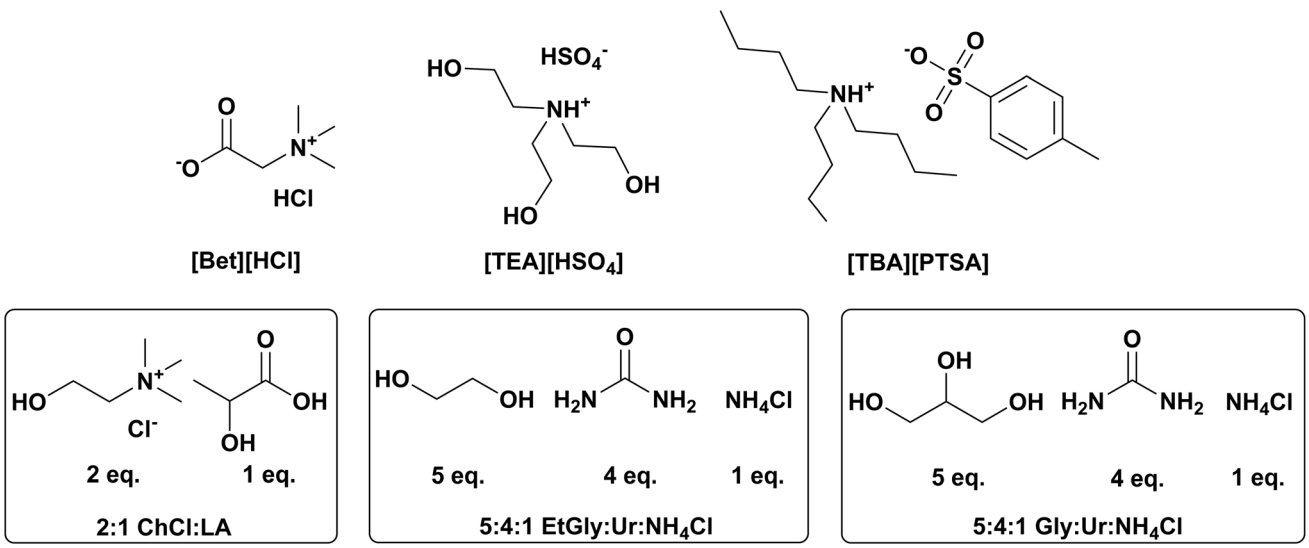

Fig. 1 Ionic liquids (top) and deep eutectic solvents (bottom) studied in this work, with their abbreviations.

increased significantly. At 30 °C, 64% of BM dissolved in 2 h, rising to 67% in 24 h, while at 80 °C the dissolution was 69% in 2 h, rising to 91% in 24 h. For all experiments with 1 M H_2SO_4, ICP-MS revealed no metal selectivity in the leachates (see the SI for extraction values); at 30 °C, the solution was saturated at 2 hours while at 80 °C there is an increase in solubility up until 24 hours, leading to almost complete dissolution of the BM. It is therefore clear that an acidic solvent (here 1 M H_2SO_4) achieves high solubilisation rates, although without any selectivity for the metals of interest. When 1 M NaOH was used as the extraction solvent, both extraction time and temperature had negligible effects on the metal leaching, as we observe 18–20% dissolution in all cases. ICP-MS revealed that NaOH extracts only small amounts of Fe from the BM (see the SI, Table S1), while the remaining lost mass is attributed to PVDF binder depolymerisation and dissolution,[25] which are known to occur in NaOH. Next, we explored the potential of ionic liquids, as extraction solvents, to improve target metal selectivity.

Extraction with aqueous protic ionic liquids

To explore the potential of aqueous protic ionic liquids in BM solubilisation, H_2SO_4 was replaced by acidic ionic liquids. First, a 30% w/w aqueous solution of betaine hydrochloride ([Bet][HCl]) was tested [Bet][HCl] was selected because it is a non-hazardous, zwitterionic compound with high water solubility and, together with choline which will be studied later, are common components of deep eutectic solvents.[26] 30% w/w is close to the limit of aqueous solubility of [Bet][HCl] and, although it yielded a significantly less acidic solution compared to 1 M H_2SO_4 (pH 2 compared to pH near 0), a very similar leaching profile was observed (Fig. 2). At 30 °C, BM dissolution is ~65% (almost identical to 1 M H_2SO_4), while at 80 °C [Bet][HCl] achieves maximum dissolution of 81% after 24 h, compared to the 91% achieved by 1 M H_2SO_4. Leaching with less concentrated solutions (10% [Bet][HCl]) was also explored but showed no improvement in selectivity (see SI Table S2). Although [Bet][HCl] is significantly less hazardous than H_2SO_4, its high production costs and the lack of cost-effective recycling processes (being zwitterionic, non-volatile and insoluble in most organic solvents) do not indicate any clear advantage as an extraction solvent.

Further studies were performed using a 30% w/w triethanolammonium hydrogen sulfate ([TEA][HSO_4]) aqueous ionic liquid solution as the extraction solvent. Triethanolammonium was selected as the cation because (a) it is a non-hazardous material and (b) it is known to be a chelating amine, forming coordination complexes with several transition metals,[27] so it would be expected to boost the solubility capacity of the solution. Fig. 2 demonstrates that, at 30 °C, the leaching profile of [TEA][HSO_4] is, like [Bet][HCl], almost identical to that of H_2SO_4; at 80 °C however [TEA][HSO_4] achieves 94% BM dissolution within 2 h, higher than that of H_2SO_4 at 24 h. The case of [TEA][HSO_4] demonstrates that introducing a chelating amine to the extraction system can significantly accelerate the dissolution rates and reduce the reaction time. This is an important finding particularly if complete dissolution of the solid matrix is required; however as the target of this study was to explore solvents that can selectively dissolve target metals, instead of completely dissolving the sample, this was not explored further.

Subsequent experiments were then designed to compare efficiency against the best extraction parameters of [TEA][HSO_4], 80 °C for 2 h. A selection of ionic liquids and deep eutectic solvents with different polarities and acidities were tested, in order to evaluate selective extraction of either Mn or Zn (Fig. 3). 30% tributylammonium *p*-toluenesulfonate ([TBA][PTSA]) was tested, as previous publications indicated that PTSA-based ionic liquids and deep eutectic solvents are promising for the extraction of Zn from waste matrices;[28,29] however, in this study no improved selectivity was observed compared to 30% [Bet][HCl]. 2 : 1 choline chloride : lactic acid (2 : 1 ChCl : LA) is a widely reported deep eutectic solvent with potential applications in the extraction of metals from several matrices;[30,31] its benefits lie in its relatively low viscosity compared to other deep eutectic solvents and the non-hazardous nature of its constituent components. In both 30% [TBA][PTSA] and 2 : 1 ChCl : LA, the mass loss during BM treatment was high (~90%) and, as a consequence, no leaching selectivity was observed. These results demonstrated that when an acid is present in the solvent (HCl, H_2SO_4, PTSA, LA) selectivity is low, likely because for all the studied solvents, the acids exist either in their neutral form

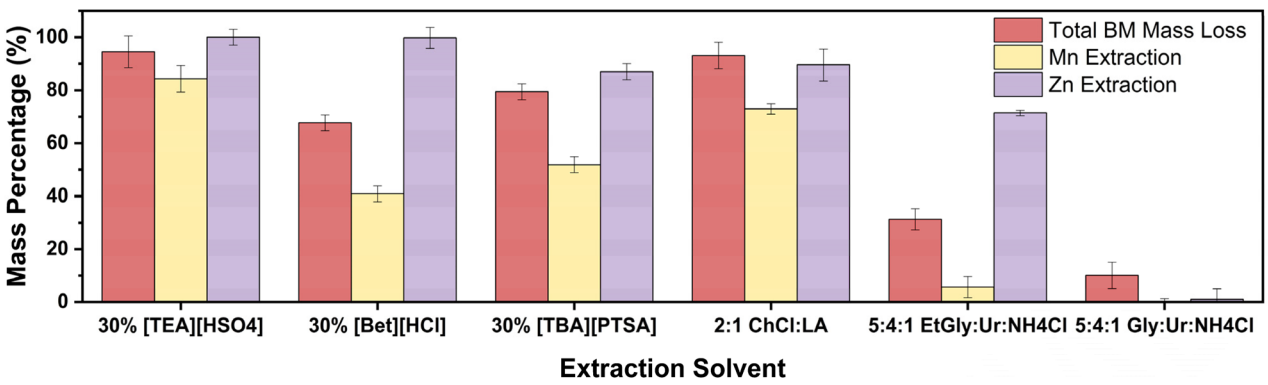

Fig. 3 Results of extractions performed with different solvent systems at 80 °C for 2 h. In red: total mass loss percentage from the original BM after leaching; in yellow and purple: Mn and Zn extraction yield from BM accordingly.

(in [Bet][HCl] and 2 : 1 ChCl : LA) or in an equilibrium between the neutral and ionic forms[21] (in protic ionic liquids [TEA][HSO_4] and [TBA][PTSA]), which makes the acidic hydrogen readily available to react with the metals present in BM and dissolve them without preference. The presence of amines demonstrated a clear impact on BM dissolution, causing a gradual dissolution at lower temperatures (compared to 1 M H_2SO_4 and HCl which non-selectively dissolve 75–90% of the BM), but their effect was not sufficient to compensate for the acid effect.

Extraction with deep eutectic solvents

Building on previous results, we explored a deep eutectic solvent that did not contain a mineral or organic acid, 5 : 4 : 1 ethylene glycol : urea : ammonium chloride (5 : 4 : 1 EtGly : Ur : NH_4Cl). This solvent would be expected to have high selectivity towards Zn, because it is basic in nature and because of the presence of NH_4^+ ions, which are known to form soluble Zn complexes under basic conditions.[32] Indeed, 5 : 4 : 1 EtGly : Ur : NH_4Cl demonstrated ~32% BM dissolution, leaching 71% of the Zn, but only 5% of the Mn from BM (leachate contains 3.0 ± 0.2 mg mL^{-1} Zn, 0.27 ± 0.05 mg mL^{-1} Mn and 0.12 ± 0.02 mg mL^{-1} Fe). The selectivity of 5 : 4 : 1 EtGly : Ur : NH_4Cl towards Zn was a significant finding, as it can provide a starting point for the design of task-specific ionic liquids and deep eutectic solvents for the targeted leaching and separation of Zn from polymetallic waste.

Two components of this deep eutectic solvent, ethylene glycol and ammonium chloride, are classified as hazardous substances (acute toxicity, level 5, H302).[33,34] To engineer a less hazardous extraction solvent, we replaced ethylene glycol with glycerol (classified as non-hazardous),[35] creating the 5 : 4 : 1 glycerol : urea : ammonium chloride (5 : 4 : 1 Gly : Ur : NH_4Cl); this led to a dramatically reduced extraction yield (~10%) and a loss of Zn selectivity (not shown in Fig. 3, but only Fe was extracted with 5 : 4 : 1 Gly : Ur : NH_4Cl). In order to understand whether this was a result of different chemical interactions, or a mixing/viscosity effect, the viscosity of the two deep eutectic solvents was measured at 80 °C, showing 12 ± 1 mPa*s for 5 : 4 : 1 EtGly : Ur : NH_4Cl and 17.3 ± 0.3 mPa*s for 5 : 4 : 1 Gly : Ur : NH_4Cl. Although the viscosities of the two solvent are different, 5 mPa*s is highly unlikely to be the single cause of such loss in selectivity. This indicated that ethylene glycol was a crucial component for the Zn extraction selectivity and further in-depth exploration is warranted, but this goes beyond the scope of this study.

Combining the findings of this study, we created a two-step process for the selective extraction and separation of Mn and Zn from BM (Fig. 4). This process involves treatment of BM with 5 : 4 : 1 EtGly : Ur : NH_4Cl, followed by treatment with 30% [TEA][HSO_4]. This route (Fig. 4) produced two leachates: S1, rich in Zn (3.0 ± 0.2 mg mL^{-1} Zn, 0.27 ± 0.05 mg mL^{-1} Mn and 0.12 ± 0.02 mg mL^{-1} Fe), and S2, rich in Mn (1.2 ± 0.1 mg mL^{-1} Zn, 4.0 ± 0.3 mg mL^{-1} Mn and 0.40 ± 0.04 mg mL^{-1} Fe). Further treatment of S1 and S2 (*e.g. via* liquid–liquid extraction or *via* selective precipitation) could be employed for further purification of these leachates; however, this is beyond the scope of this work. This short communication has demonstrated that component selection in ionic liquids and deep eutectic solvents can indeed lead to selective extraction of critical metals from BM. The project will continue in the future with a full, systematic study, including complete process optimisation life cycle assessments of the chemical involved.

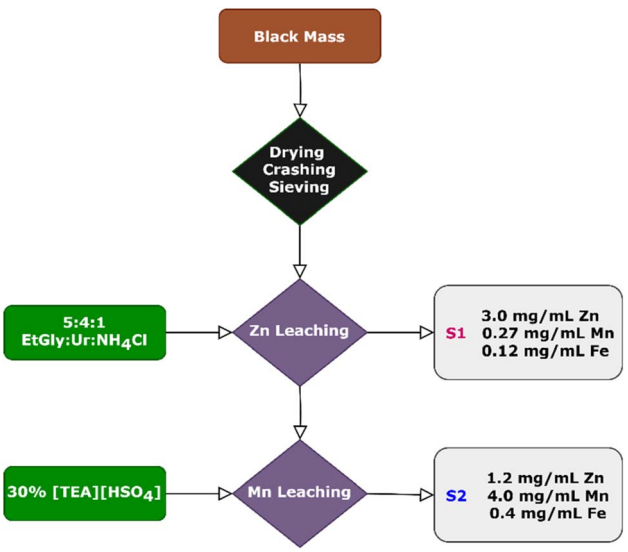

Fig. 4 Two-step process for the extraction of Zn and Mn from alkaline battery BM. The complete process achieves 100% Zn leaching, 79% Mn leaching and 98% Fe leaching.

Conclusions

In this work we explored the potential of aqueous protic ionic liquids and deep eutectic solvents for the leaching of Zn and Mn from BM of alkaline batteries. We have demonstrated that with careful selection of the ionic liquids' and deep eutectic solvents' constituents, selective leaching of the target metals is achievable. When acidic protic ionic liquids and deep eutectic solvents are used, dissolution is high (80–95% depending on the solvent), but selectivity remains low, due to the high reactivity of the available acidic protons towards the metals contained in the BM powder. However, changing to deep eutectic solvents with basic components, such as 5 : 4 : 1 EtGly : Ur : NH_4Cl, achieved high selectivity and yield in Zn leaching (71% leaching yield on Zn, while only 5% leaching on Mn). These results are very promising and a complete, systematic study of such solvent systems is urgent, particularly in light of the observation that modification of the solvent with components with theoretically similar chemical profiles (*e.g.* replacing ethylene glycol with glycerol) demonstrated dramatic effects on the extraction efficiencies. Finally, as discussed in the Introduction, the bottleneck in the commercialisation of such technologies is their economic viability, so performing techno-economic analyses to evaluate the viability of such solvent systems is crucial. Finally, emphasis is currently placed on developing more efficient and sustainable processes for the stripping of the metals from the

leachates (*e.g.* liquid–liquid extraction or electrowinning), which will allow for the recycling and reuse of the solvent.

Author contributions

Conceptualisation: F. P. R., F. M.; supervision: S. K., F. P. R., F. M.; investigation: C. L., K. K., T. L., S. K.; methodology: C. L., K. K., S. K.; writing – original draft preparation: S. K., C. L.; writing – review & editing: S. K., F. P. R., F. M.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: materials and methods, pre-treatment of BM, synthesis of ionic liquids and deep eutectic solvents, ^{1}H NMR and ^{13}C NMR spectra of ionic liquids, extraction of BM with [Bet][HCl] and [TEA][HSO_4] with varying water contents, extraction of BM with 5 : 4 : 1 EtGly : Ur : NH_4Cl with varying temperatures and extraction times. See DOI: **https://doi.org/10.1039/d5su00737b**.

Acknowledgements

The project was funded as part of the Department for Science, Innovation & Technology (DSIT), within the UK India Critical Minerals Partnership – Phase 2 project and administered *via* CPI's Innovation Sprint Competition relating to Critical Minerals Manufacturing Technologies. The authors thank Dr Athan Fox from Ever Resource Ltd for providing the BM. We also thank the Chemical Engineering Analytical Suite of Imperial College London (ICP-MS, XRD and XRF) and The Henry Royce Institute (Royce Imperial) for providing access to their analytical equipment (SEM/EDX).

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