Title	Harnessing the complexity: Deep Eutectic Solvents for selective metal recovery (HarCo)

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# months (min.3)	6

Project description (2 page max):

Within the broad framework of Circular Economy, aiming at developing efficient approaches for recovery of valuable resources to be used as secondary raw materials in production processes, and considering the very recent policies implemented by the European Union in relation to **critical and strategic raw materials** (see for instance the Critical Raw Materials Act, 2023)[1], the present PhD research project aims to discover new, sustainable and cost-effective solvents, obtained from abundant precursors, enabling the selective extraction of desired components form complex matrices. In particular, new types of sustainable **Deep Eutectic Solvents (DES)**[2] will be devised for their use in two strategic applications: i. recovery of two critical metals, namely lithium and cobalt from black mass derived from spent batteries and ii. recovery of a strategic metal[1], i.e. copper, from Waste Electrical and Electronic Equipment (WEEE).

DES are an emerging class of compounds, mostly consisting of **suitable hydrogen bond donors (HBD)/acceptors (HBA) pairs**. When mixed in appropriate molar ratio, the HBA and HBD components form a eutectic mixture with a lower melting point than individual components. DES are often acknowledged as a new generation of ionic liquids (ILs), since they share with them the advantages of good thermal (suitable for to microwave irradiation) and chemical stability, tuneable properties (by varying compositions), low vapour pressure, non-flammability, strong solubilisation power. Moreover, they exhibit other appealing features, such as easier preparation methods (typically relying on simple mixing at room or low temperature), lower cost, lower corrosivity and, in general lower toxicity with respect to ILs. They have been implemented for very different applications, ranging from extraction and separation of various compounds, metal plating, biomass processing, synthesis of inorganic nanomaterials, gas adsorption, use as electrolytes[3].

The planned application, i.e. the **selective metal recovery**, represents an extremely urgent issue. Due to rapid development of global economy and increase in world population, the demand for metals is continuously increasing, while many countries worldwide are facing metal scarcity, and the critical raw materials list for Europe is widening, encompassing not only well-established critical metals (e.g., Li) but also strategic metals (e.g., Cu)[1]. The recovery of metals from **complex waste mixtures** is typically accomplished through pyrometallurgical or hydrometallurgical processes[4], which are however characterised by a high impact in terms of need of high temperatures and use of highly corrosive and toxic lixiviants.

In this context, DES might represent a versatile, sustainable and appealing solvometallurgical alternative for different reasons: i. they effectively solubilise a broad range of metals and metal oxides, making possible to use them for the **leaching of metals from primary or secondary resources**; ii. they have a large electrochemical window, which allows the application of electrochemical techniques such as electrodeposition to refine metals; iii. additionally hydrophobic DES (HDES) can be used for the extraction of metal ions from aqueous solutions, thus implementing the recovery (ad DES recycling) steps.

The **PhD project** entails preparation, characterisation, properties screening of the DES, followed by validation activities focused on their application within two case studies. As precursors, inorganic salts based on earth-abundant and less common metals and widely available organic compounds (e.g. urea, carboxylic acids etc.) will be screened, also using water as a third component to lower the viscosity. A comprehensive **exploration of the full experimental parameters space** (i.e. chemical nature and molar ratios of HBA and HBD; possible broadening to ternary formulations, including the addition of water; physical methods of preparation; temperature of preparation, with possible use of subcritical hydrothermal treatments) will be performed by **Design of Experiment**[5] and correlated to the resulting physico-chemical and functional prop-

[1] Critical Raw Materials Act, (2023) European Commission, COM(2023) 165 final

[2] Abbott et al. Preparation of novel, moisture-stable, Lewis-acidic ionic liquids containing quaternary ammonium salts. Chem. Commun. 2010 (2001). Smith et al. Deep Eutectic Solvents (DESs) and Their Applications. Chem. Rev. 114, 11060 (2014)

[3] Jenkin et al. Miner. Eng. 87, 18 (2016). Abbott et al. J. Chem. Eng. Data 51, 1280 (2006). Hammond et al. Chem. Commun. 58, 3865 (2022); Ko, J. et al. ACS Appl. Energy Mater. 7, 850 (2024);

[4] Zante et al. Review on Hydrometallurgical Recovery of Metals with DES. Sustain. Chem. 1, 238 (2020)

[5] S. Gross et al. Design of Experiment: A Rational and Still Unexplored Approach to Inorganic Materials' Synthesis Sustainable Chemistry, 2022, 3(1), 114-130

erties of the DES determined by a multi-analytical characterisation approach complemented by **modelling**. In particular, acidity, coordination ability, and reducibility of the DES represent key properties to achieve better dissolution of metal oxides. On the other hand, a low viscosity is highly desirable to promote mass transfer and diffusion.

Studies of fundamental nature will be directed to investigate, from a chemical-physical and structural point of view, the properties of these systems, to determine the nature of the interactions underlying their formation (with support of quantum Density Functional Theory (DFT) calculations delivered within a scientific cooperation with Prof. Laura Orian) and their functional and rheological behavior as a function of temperature (phase diagram, extraction efficiency/selectivity). **Design of Experiment (DoE), combined with Machine Learning (ML) approaches** (these latter in cooperation with Prof. Antonino Polimeno and Dr. Sergio Rampino) will be applied for exploring the experimental parameters space and for **accelerated discovery of new formulations with desired properties**[6]. Particularly promising in this respect is the growing field of generative ML models, which have recently proven to successfully address complex forward and inverse design problems in molecular modelling and design. Generative neural-network models can be trained to generate *de novo* molecular systems that meet a set of desired behavioural properties, thus providing a framework for both understanding DES and discovering new DES.

Optimised DES will then be tested in the selected applications by using materials delivered, in the case of spent battery, by the company STIGA (Castelfranco Veneto), whereas the WEEE materials will be recovered by a "Centro RAEE" in Padova, upon specific agreement with APS-Acegas (Padova). Although the extraction of selected metal ions will represent a major goal, the isolation of mixed oxides as $LiCoO_2$ (a valuable cathode material) as output materials will be also possible. In this case, thermal treatments, electrodeposition, precipitation strategies will be applied to separate and collect the single ions.

The PhD project, developing within three years, will be organised according to the following time-schedule and will encompass also a 6 months secondment at University of Leiecester, in the group of Prof. Andy Abbot, **the most renowned scientist in the field of DES**, with whom the two co-proponents have already some preliminary contacts and planned collaborations.

TIME DEVELOPMENT OF THE PHD PROJECT

M1-M2	bibliographic and patent search to enable freedom to operate (FtO)
M2-M12	**DoE-supported synthesis and multi-analytical characterization** of different DES formulations for the two targeted applications
M2-M12	DFT and experimental studies on HBA/HBD interactions (cooperation Prof. L. Orian)
M13-M24	validation of separation and selectivity on targeted solid waste and **accelerated materials discovery by machine learning** (cooperation Prof. A. Polimeno- Dr. S. Rampino)
M24-M30	secondment at University of Leiecester for advanced characterisation and up-scale of the most promising formulations developed in Padova
M30-M36	final optimization of DES best performing formulations, data analysis, writing of thesis and publications

The two co-proponents are already cooperating since 2022 on the topic and Gross is already working on copper recovery by sustainable approaches (i.e., carboxylic acid and salts, work carried out by PhD student P. Ostellari and Master students M. Tapparelli and A. Gazziero). A Master thesis (Z. Smania) in Industrial Chemistry on DES has been finalised in 2023. Additionally, preliminary tests (fellowship performed in Carraro's group) are ongoing on the use of DES to extract metals from Li battery (black mass). The two co-proponents share all synthesis (sonicators, microwave ovens) and analytical methods (ATR, UV-Vis, rheometer, ICP-OES, TGA, DSC) to characterise the DES and quantify metal extraction efficiency. They share lab spaces and activities. This will ensure to the PhD student an optimal research environment and mentorship.

[6] Mohan et al. Accurate prediction of carbon dioxide capture by DES using quantum chemistry and a neural network. Green Chem. 25, 3475 (2023); Gómez-Bombarelli, et al. Automatic Chemical Design Using a Data-Driven Continuous Representation of Molecules. ACS Cent. Sci. 4, 268 (2018);