Green Ionic Liquids additives in high-voltage lithium batteries

M. Palluzzi[1], *G. Mannucci*[1], *A. Tsurumaki*[1-2], *M. Busato*[1], *P. D'Angelo*[1], *M. A. Navarra*[1-2]

[1]*Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro, 00185 Roma, Italy.*

[2]*Hydro-Eco Research Center, Sapienza University of Rome, Via A. Scarpa 16, 00161 Rome, Italy*

matteo.palluzzi@uniroma1.it

A key goal in battery research is to enhance the energy density of lithium-ion batteries (LIBs) while ensuring safety, sustainability, and low cost. Achieving this requires a transition to new cathode materials that operate at higher potentials than traditional ones like $LiCoO_2$. $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) is particularly promising due to its high operating voltage of 4.7V vs Li^+/Li and its cobalt-free composition. However, its commercial use is limited by the incompatibility of conventional carbonate-based electrolytes, which degrade forming HF, causing corrosion of the cathode at high potentials. To address this, electrolyte materials able to form a protective cathode-electrolyte interphase (CEI) are needed. Oxalatoborate-based ionic liquids (ILs), which contain bis(oxalato)borate or difluoro(oxalato)borate anions, can create a boron-based protective layer on the cathode surface[1,2]. However, traditional IL synthesis involves high costs and the use of environmentally harmful solvents.

This project aims to develop water-based synthesis methods for oxalatoborate ILs, overcoming the notable challenges due to their high hydrophilicity. The focus of this presentation will be on two ILs: *N*-ethoxyethyl-*N*-methylpiperidinium difluoro(oxalato)borate ($PIP_{1,2O2}$DFOB) and *N*-ethoxyethyl-*N*-methylpiperidinium bis(oxalato)borate ($PIP_{1,2O2}$BOB). These ILs were characterized using spectroscopic methods, and their thermal properties were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), aiming to ensure their thermal stability for the use in battery devices. Molecular dynamics and DFT calculations explained the observed thermal behaviors. Finally, results demonstrating their compatibility with LNMO cathodes in Li||LNMO systems will be presented.

References

1. Tsurumaki, A., Branchi, M., Rigano, A., Poiana, R., Panero, S., and Navarra, M.A. (2019) Bis(oxalato)borate and difluoro(oxalato)borate-based ionic liquids as electrolyte additives to improve the capacity retention in high voltage lithium batteries. *Electrochimica Acta*, **315**, 17–23.

2. Palluzzi, M., Tsurumaki, A., Mozhzhukhina, N., Rizell, J., Matic, A., D'Angelo, P., and Navarra, M.A. (2024) Ionic Liquids as Cathode Additives for High Voltage Lithium Batteries. *Batteries & Supercaps*, e202400068.

Acknowledgments
This work has been financed by the Research Fund for the Italian Electrical System under the Three-Year Research Plan 2022-2024 (DM MITE n. 337, 15.09.2022), in compliance with the Decree of April 16th, 2018".