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Holes, Hops and Haven Ratios—Molecular Dynamics of Ion Transport and Transference in MFSI/[C_4C_1pyr][FSI] electrolytes (M = Li, Na, K)

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Room-temperature ionic liquids (ILs) are molten salts with negligible vapour pressure and wide electrochemical windows, making them attractive electrolytes for beyond-lithium batteries [1]. Optimising transport properties—such as conductivity, self-diffusion, and the working-ion transference number (the fraction of the total ionic current carried by Li^+/Na^+/K^+ from the added salt)—requires further quantitative, molecular-scale insight into how charge and mass move. Equilibrium molecular dynamics (MD) provides this insight by enabling transport coefficients and mechanistic signatures to be extracted from atomistic simulations. The rate capability of a battery is tightly coupled to the transport properties of the electrolyte; formulations that raise the working-ion transference number while maintaining adequate conductivity are preferred [2].

In this work, MD simulations were used to probe 1-butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide ([C_4C_1pyr][FSI]) mixed with MFSI (M = Li, Na, K) at salt mole fractions of 0.10, 0.20, 0.40 and T = 348.15 K. A non-polarisable model based on the well-established CL&P force field was employed [3]; however, non-bonded interaction parameters were adjusted to better reflect symmetry-adapted perturbation theory (SAPT) decomposition of pairwise interactions, including cation–anion and metal-salt pairs. Equilibrium trajectories of ≥250 ns per state point were generated with LAMMPS [4]. Self-diffusion coefficients were obtained from Einstein mean-squared displacements, and ionic conductivity was computed using the Green–Kubo/Einstein–Helfand formulation. The analysis includes Nernst–Einstein estimates of conductivity (σ_{NE}), Haven ratios (σ_{NE}/σ) and its inverse (ionicity, σ/σ_{NE}), and both apparent transference numbers (from self-diffusion coefficients) and real/collective transference numbers from conductivity decomposition in an Onsager framework. Mechanisms of ion transport are examined via Van Hove correlation functions (self and distinct), the non-Gaussian parameter, ion–anion residence times, and coordination numbers. Hole (free-volume) theory is evaluated as a compact model for conductivity across composition.

HPC Content: Strong scaling was assessed for fixed-size systems of 256, 512, and 1024 ion pairs on 1–64 CPU cores (MPI ranks); wall-time per ns and ns/day were recorded to determine speedup and parallel efficiency. For one representative state point, transport properties are compared across these system sizes to illustrate finite-size effects.

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[3] Canongia Lopes, J. N.; Pádua, A. A. H., CL&P: A generic and systematic force field for ionic liquids modeling. *Theor. Chem. Acc.* **2012**, *131*, 1-11.
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Presenting Author

Gerhard Venter

Email

gerhard.venter@uct.ac.za

Student or Postdoc?

No. Not a student nor Postdoc.

Institute

University of Cape Town

Registered for the conference?

No

CHPC User

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