

THERMOELECTROCHEMISTRY FOR HARVESTING WASTE HEAT

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Current devices to harvest heat have significant limitations, and typically consist of intricate mechanical systems, such as either a petrol engine or a steam turbine. Thermochemistry is a simple, scalable technique for the direct electrochemical conversion of thermal energy into useful electricity.^{1, 2} It is driven by the entropy change associated with a redox process, resulting in a temperature dependence of the electrode potential (the Seebeck effect).¹ The greater this dependence (the larger the Seebeck effect) the more efficient the power generation through this method.³ If there is a temperature difference between two identical electrodes, this difference can be converted into electricity using electrochemistry; such systems are ideal for harvesting low-grade heat that would otherwise go to waste.² Ionic liquids have solvent properties appropriate for thermochemistry systems such as wide liquid temperature ranges, low vapour pressure, low flammability and favourable interactions with charged, redox active species which can lead to a large entropy change.²

Given the above benefits we have investigated the thermochemistry of lithium-glyme based solvate ionic liquids using mixtures of lithium bis(trifluoromethylsulfonyl)imide ($\text{Li}[\text{Tf}_2\text{N}]$) in various glymes (monoglyme, diglyme, triglyme and tetraglyme³) as well as tetrahydrofuran (THF). The process is entropically driven by the formation of a lithium-glyme or lithium-THF complex on the cold electrode accompanied by the release of an electron, and the release of the lithium from the complex at the hot electrode accompanied by the capture of an electron and deposition of lithium (Figure 1). By investigating the properties of these solvated ionic liquids, we have been able to identify optimized solvent conditions for this application.

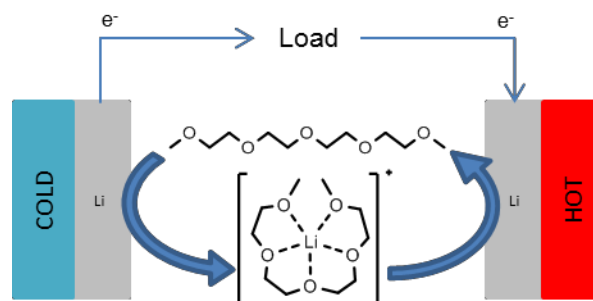


Figure 1. Schematic of one of the thermochemistry processes considered

An alternative redox couple to consider for utilization of waste heat is corannulene (Figure 2) and its reduced forms. Corannulene is a non-planar, polycyclic, aromatic hydrocarbon with several known redox states capable of undergoing a bowl to bowl inversion.⁴ It is hypothesized that small cations such as lithium are able to interact with corannulene anions⁵ and hinder the bowl to bowl inversion upon formation of the anion. Such an interaction would result in a large Seebeck effect making it desirable to investigate in terms of harvesting waste heat. Therefore we have investigated the thermochemistry of corannulene in a range of different solvents including several ionic liquids.

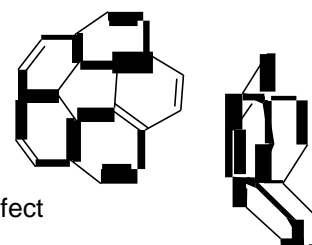


Figure 2. Corannulene

References

1. P. Gründler, A. Kirbs and L. Dunsch, *ChemPhysChem*, 2009, 10, 1722-1746.
2. T. J. Abraham, D. R. MacFarlane and J. M. Pringle, *Chemical Commun.*, 2011, 47, 6260-6262.
3. J. J. Black, T. Murphy, R. Atkin, A. Dolan and L. Aldous, *Phys. Chem. Chem. Phys.*, 2016, 18, 20768-20777.
4. M. Baumgarten, L. Gherghel, M. Wagner, A. Weitz, M. Rabinovitz, P. C. Cheng and L. T. Scott, *J. Am. Chem. Soc.*, 1995, 117, 6254-6257.
5. S. N. Spisak, A. V. Zabula, M. V. Ferguson, A. S. Filatov and M. A. Petrukhina, *Organometallics*, 2013, 32, 538-543.