Poster

Utilizing structural studies for developing a new concept of aqueous electrolytes based on lithium 4,5-dicyanoimidazolate hydrates

M. Dranka[1], M. Fabiański[1], A. Zalewska[1] G. Z. Żukowska[1], W. Wieczorek[1]

[1]Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warszawa, Poland

maciej.dranka@pw.edu.pl

The increasing focus on safety in battery technology has directed much of the research towards batteries with aqueous electrolytes or electrolytes with water added. The salt concentration level in the electrolyte system is crucial to modifying the solvated structure of lithium cation due to the inactivation of water molecules. While water-in-salt electrolytes show promise, it's important to note that research in this field is ongoing, and challenges such as achieving long cycle life and maintaining performance at high rates still need to be addressed for practical implementation in commercial battery technologies. Unfortunately, our understanding of the microscopic-level local structure of electrolytes remains quite limited. Insight into the solvation of Li^+ cations and the mechanisms of their aggregation is essential due to their crucial roles in ionic conductivity and the formation of a solid electrolyte interface (SEI). Among various salts containing stable organic fluorine atoms, which will not undergo hydrolysis, the heterocyclic Hückel anions such as 4,5-dicyanoimidazolate (TDI) attract the interest. Lithium salt of TDI (LiTDI) was successfully used as the moisture-scavenging agent, but the mechanism is still unknown [1]. Our previous experience in structural research of heterocyclic salts allowed us to systematically determine preferred coordination modes in LiTDI–H_2O systems [2]. LiTDI salt in water solution can form several hydrates of composition $LiTDI \cdot xH_2O$ (where x=1-4) depending on the concentration and temperature. Our recent structural studies showed that dimeric lithium 4,5-dicyanoimidazolate (LiTDI) dihydrate molecules, in the presence of acetonitrile (AN), form an ionic system preserved in high concentrations and solid states (Fig. 1). X-ray diffraction measurements demonstrate that electroneutral dihydrate units can coordinate additional lithium cations acting as charge carriers. Utilizing this finding, a new concept of aqueous electrolytes based on heterocyclic anions (hydrated anionic triplet electrolytes) has been advised. The crystalline ionic phase was characterized using spectroscopic, thermal, and electrochemical methods and was used to prepare model electrolytes based on LiTDI hydrates. Linear sweep voltammetry and impedance spectroscopy measurements confirm, in this system, the depletion of water activity, high conductivity, and reversible cycling of full cells comprising examined electrolytes. We will prove that a concentrated triplet solution acts similarly to the anhydrous electrolyte; regardless of the concentration, it reaches high ionic conductivity values (12-16 mS/cm at room temperature) and is electrochemically stable.

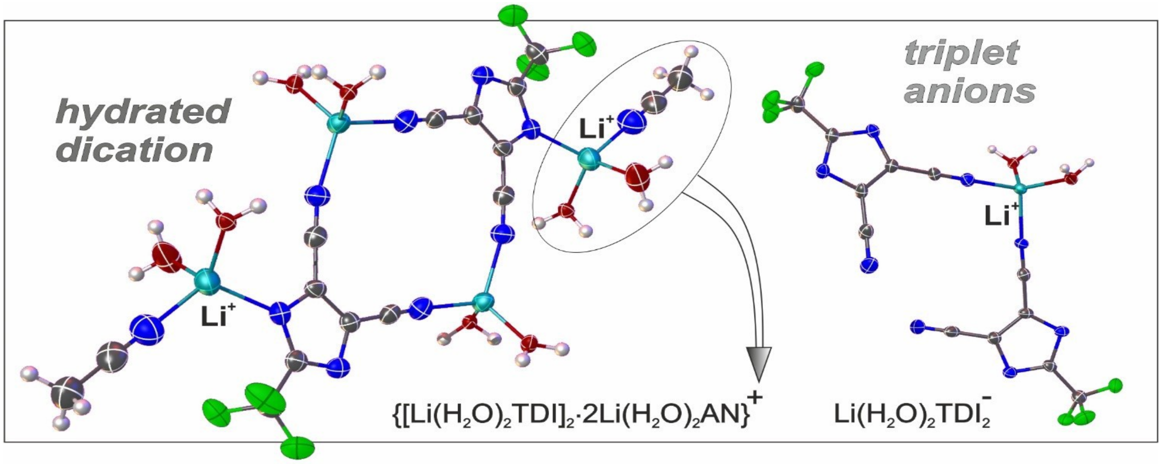

Figure 1. The solid-state structure of the ternary LiTDI-H_2O-AN system shows stable dications and anionic triplets.

[1] Xu, C., Renault, S., Ebadi, M., Wang, Z., Björklund, E., Guyomard, D., Brandell, D., Edström, K. & Gustafsson, T. (2017). *Chem. Mater.*, **29**, 2254.

[2] Dranka, M., Jankowski, P. & Żukowska, G. Z. (2018). *J. Phys. Chem. C*, **122**, 3201.