

New Salts for Sodium-Ion Batteries

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The first successful attempt of a sodium battery was undertaken in 1967 by Ford Motor Company (USA) in the sodium-sulfur battery. This innovation was possible from to the discovery by Ford researchers of the favourable Na⁺ ionic conduction properties in β-alumina. The growing application of Li-ion and Li-polymer batteries for hybrid electric cars, electric vehicles, mobile devices etc. requires a large amount of lithium in the form of Li₂CO₃ every year. High price and relatively small world reserves of 13 million tons, forced to look for new materials possible to use in battery technology.

Sodium has molar mass and only slightly lower than lithium red-ox potential (2.73V). Low cost (about 4 times lower than lithium) and enormously easier and almost unlimited world-wide reserves makes him a really promising candidate. Metallic sodium does not form dendrites being a key issue if lithium metallic anodes (with gigantic theoretical capacity of 1190 mAh/g) were tested in present batteries. Several secondary advantages only promotes sodium concept for ex. cheaper than aluminum current collectors might be applied. [1]

The challenge in development of sodium battery technology is to shift temperature of work to room temperature by careful choosing of the salt, what includes anion designing. The anion modification should consider present of specific elements (carbon, nitrogen, optionally fluorine) related to low toxicity and electrochemical resistance, and moreover uniform charge distribution, which courses good dissociation and in consequence high ionic conductivity.

The novel, promising concept of the application of new anions is based on the application of "Hückel anions". The name came from the transposition of the Hückel rule predicting the stability of the aromatic systems. One of the most common examples of this type of anions is 4,5-dicyano-triazole (DCTA). This particular structure is completely covalently bonded and shows very stable 6π (or 10π electron if CN bonds are involved in calculations) configuration. It can be produced from commercially available precursor and even more importantly does not comprise fluorine atoms. Salts of this type of anion were found to exhibit high (~300°C) thermal stability. LiDCTA was successfully tested in PEO matrices systems as a promising, improved electrolyte for rechargeable lithium batteries [2]. Unfortunately DCTA failed as a component of the EC/DMC (1:1) battery electrolyte.

This paper presents the properties of newly designed sodium salts e.g. sodium 4,5-dicyano-2-(trifluoromethyl)imidazolate (NaTDI) and sodium 4,5-dicyano-2-(pentafluoroethyl)imidazolate (NaPDI) for application in liquid non-aqueous sodium electrolytes.

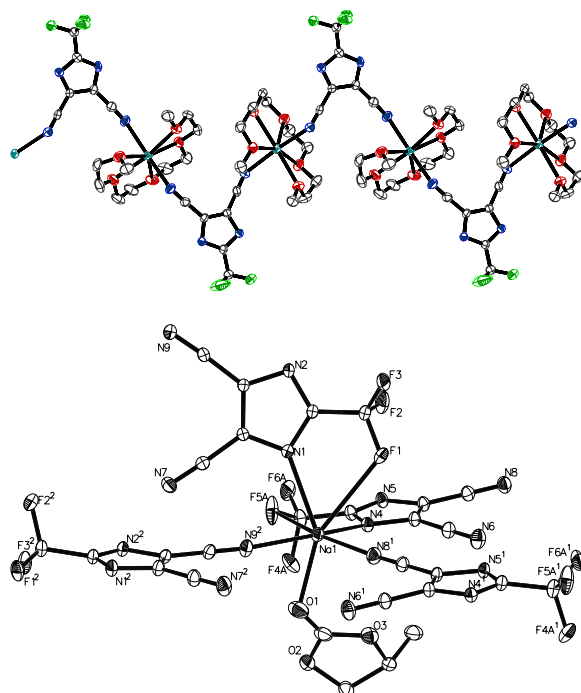


Fig. 1 Structure of tetraglymeNaTDI and PCNaTDI.

For the very first time new sodium salts with five-membered ring imidazolium anion were synthesized. Salts were found extremely stable up to more than 300°C (TGA). Moreover interesting properties of synthesized salts and their solutions in the PC solvent were proven by structural characteristic, electrochemical testing and Raman spectroscopy. NaTDI and NaPDI based electrolytes in PC show good conductivity with the values about 4mS⁻¹ at 20°C for salt concentration 0.5M and 1M for both salts and can be enhanced by optimization of salt concentration and solvent composition. Ionic conductivities collected for both salts are almost the same considering slope over temperatures and pure values. Interestingly the high values of the conductivities are reached for 0.5M salt concentrations which is extreme advantage if we consider material savings. Superior properties were also confirmed by Raman spectroscopy used for the ionic association monitoring. Raman spectroscopy showed excellent salts dissociation in carbonate as PC and absence of ion-pairs for concentration up to 0.5M. Combining this with thermal stability over 300°C plus the elevated electrochemical stability over 4.5V for NaTDI and 4.2V NaPDI vs Na/Na⁺ makes these salts interesting as a candidate for electrolyte's sodium salt carrier.

[1]. A. Eftekhari, *J. Power Sources* 126 (2004) 221-228

[2]. M. Egashira, B. Scrosati, M. Armand, S. Béranger, C. Michot, *Electrochem. Solid-State Lett.* 6 (2003) A71.