

Dinitrile-based Electrolytes for high voltage Lithium-Ion Batteries

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Recent studies showed that electrolytes based on aliphatic dinitriles, $\text{NC}-(\text{CH}_2)_n-\text{CN}$, $n = 3-8$, have the desired properties that make them suitable for lithium-ion batteries. Aliphatic dinitriles are thermally and electrochemically stable with an electrochemical stability window up to 8 V, and in the case of the shorter alkane dinitrile, adiponitrile (ADN, $n=4$) it has good solvating ability, high boiling and flash points, commercially available and relatively cheap [1,2]. The properties of dinitriles vary with chain length such as plastic crystalline behavior, melting point, density and dielectric constant. It is therefore imperative to understand the crystal structure of the dinitrile as a function of chain length and temperature.

All the dinitriles were successfully crystallized and their structures were determined between -100 to 100 °C. All of the structures from simulated annealing were found to be correct after energy minimization. The dinitriles with even-numbered carbons tend to have higher melting points, but an additional trend became apparent with cell symmetry (Figure 1). Even-numbered dinitriles are all $\text{P2}_1/\text{c}$ although octanedinitrile has a doubled cell. Odd-numbered dinitriles show no trend. In general, an alteration in melting point between “odd” and “even” dinitriles is clear and can be attributed to a difference in packing behavior similar to aliphatic dithiols [3].

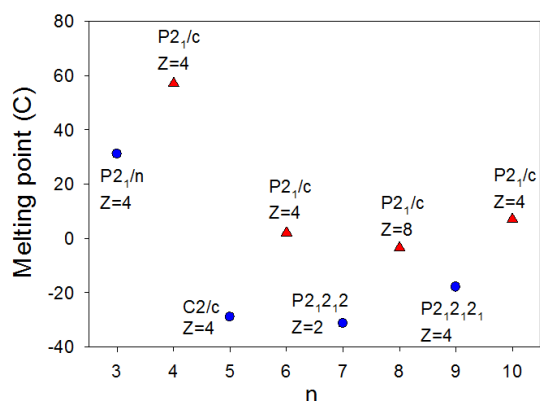


Figure 1. Variation in melting point and cell symmetry as a function of chain length

The performance of all the dinitrile solvents was evaluated in lithium batteries with the high voltage $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (4.9 V) negative electrode. It was found that a ternary electrolyte solution mixture consisting of EC: DMC: dinitrile 1:1:2 (by volume) (dinitrile = ADN, PMN, SUN and SEN) with the LiBF_4 salt and LiBOB as a co-salt were needed to obtain good cyclability [4,5].

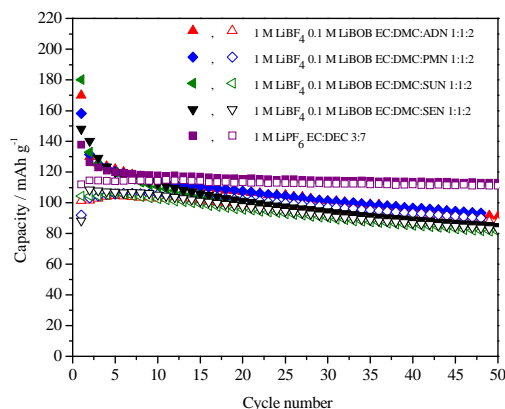


Figure 2. Charge and discharge curves of Li/ $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cells using EC:DMC:dinitrile 1:1:2 (by volume) (ADN, PMN, SUN and SEN) 1M LiBF_4 0.1M LiBOB electrolytes.

As shown in Figure 2, The initial capacities ranged from 101 mAh g^{-1} to 108 mAh g^{-1} at a C/12 rate and electrolytes with shorter alkane dinitriles having lower “ n ”: = 4 and 5 showed better capacity retention after 50 cycles than longer alkyl dinitriles with higher “ n ” = 6 and 8.

Investigation of the cathode-electrolyte surface of cycled cells by XPS revealed that large quantities of LiF were present at the surface of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ in a binary electrolyte of adiponitrile, $n = 4$, possibly explaining the low efficiency in EC: dinitrile binary electrolytes and the great role DMC plays in ternary electrolytes to passivate the surface at high voltages. An ATR IR study of the EC, DMC and ADN electrolytes showed a strong interaction between the lithium ion and the functional groups of the three solvents with higher affinity to the carbonate than the dinitrile as nitrile solvents in general have lower DN than carbonates [5]. An XRD study of certain ADN:LiTFSI complexes showed that at high concentrations crystalline complexes form with lithium tetrahedrally coordinated to the nitrile groups.

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- 4- M. Nagahama, N. Hasegawa and S. Okada, *Journal of The Electrochemical Society*, **157**, A748 (2010).
- 5- N. Salem, H. Duncan and Y. Abu-Lebdeh, *J. Electrochem. Soc.*, submitted.