

STRUCTURE-PROPERTY RELATIONSHIPS OF NAPHTHALENE DIIMIDE BASED ORGANIC ELECTRODES

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As our society continues to pursue an economic future independent of fossil fuels, it has become increasingly clear that large improvements in energy storage technologies are required. In particular, various aspects of lithium-ion batteries are being researched for concurrent improvements in cost, safety, energy- and power-density, and cycle life. While numerous recent advances in high-voltage cathodes, high-capacity alloying anodes, engineered electrode architectures and safer electrolytes have advanced the field greatly, there is as of yet no battery solution which has achieved the combination of properties necessary to significantly displace liquid fuels.

Organic compounds are enjoying a resurgence in interest as lithium-ion electrodes due to their potentially high specific energy, wide range of available structures and reaction mechanisms, and potentially low cost due to both a lack of expensive metals and ease of industrial scale manufacturing.¹ Additionally, a wide range of base structures and functional groups are available to tailor properties such as capacity, redox potential, conductivity and solubility.

In this work, we detail a class of organic electrode materials based on a family of naphthalene diimide (NDI) derivatives, and describe the structural relationship of its electrochemical performance in a lithium-ion cell. Already well characterized as an organic semiconductor², NDI can be electrochemically reduced with lithium at a potential near 2.5V vs. Li/Li⁺. [Fig. 1] Each NDI can be reduced by two electrons, for a theoretical capacity of just over 200 mAh g⁻¹ for the parent NDI.

The chief advantage of NDI as an electrode material is that the X and R groups can be chosen to adjust redox properties of NDI. The effect of R on the cycle life of NDI has been briefly addressed by Kim et al.³ with particular regard to dissolution of active material into the electrolyte. In addition, the effect of a core substitution on the redox properties of NDI has been explored by Röger et al.,⁴ but the effect of such substitutions in a lithium-ion system have not been reported in the literature.

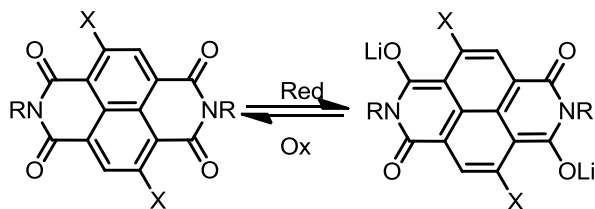


Figure 1: Redox reaction of naphthalene diimide with lithium. X can be chosen to adjust the reaction potential, and R can be selected for ease of synthesis and control of solubility.

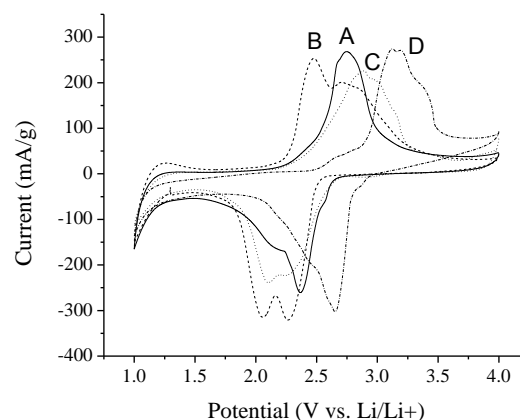


Figure 2: Cyclic voltammetry of various NDI compounds where a) R and X are both hydrogen, or where R is hexyl and X is b) hydrogen; c) fluorine; d) nitrile. Electrodes were tested in a two-electrode coin cell with lithium counter and 1M LiClO₄ EC:DMC electrolyte, at a scan rate of 1 mV/s.

We show that the redox potential of NDI can be adjusted by altering the functional group X to tailor the electronics of the process. [Fig. 2] The R group can similarly be selected independently to facilitate ease of synthesis, adjust solubility of the NDI in electrolyte, adjust theoretical capacity, and slightly shift the redox potential. We explore several different NDI derivatives, where X has been selected to be either electron donating, or withdrawing via either resonance or induction. We then detail the effect these different structures have on redox potential, capacity and cycle life. Finally, we address the potential for these compounds to be used with other battery chemistries, such as sodium-ion.

References

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