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Current cathode materials for Li-ion batteries (LIBs) are mainly composed of inorganic insertion compounds, such as $LiCoO_2$, $LiNiO_2$, Li_2MnO_4 , $LiFePO_4$ *etc.* [1], but recent surging demand for green electrodes calls for the development of novel Li-ion cathodes with the ability to deliver high capacity and also being environmental friendly. From the viewpoint of structural diversity and sustainability, organic cathodes have so far received significant research interest, which also possess many other beneficial properties, such as light weight, flexibility and easily availability [2].

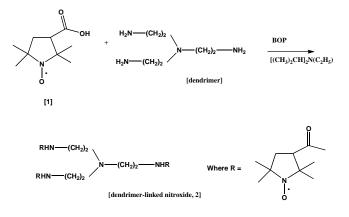


Fig.1 The synthesis process and structure of DENDN-650.

Here a dendritic-like core structure of nitroxide, dendrimer-linked nitroxide (DENDN-650) with three nitroxide units bound to the terminal amines in the dendrimer, has been successfully synthesized using the method of Winalski, *et al.*, [3], see Fig. 1. This compound has a theoretical specific capacity of 123 mAh/g. The dendrimer nitroxide cathodes were prepared by casting the mixture of DENDN-650, PVA and carbon black in a weight ratio of 70:15:15 on an Al foil current collector.

cathode The dendrimer-linked nitroxide exhibited reversible redox reactions with the plateau located at 3.5 V during the charge and discharge process in electrolyte of 3 M LiPF6 dissolved in ethylene carbonate and diethyl carbonate (EC+DEC, 1:1 V), see charge/discharge profile in Fig. 2. The possible lithiation/delithiation mechanism for this kind of organic cathode was investigated. Furthermore, a mechanism was proposed which involves Li-ion adsorption/desorption on the surface of electrodes during the charging and discharging process, which is different from current lithiation/delithiation mechanisms, such as Li-ion insertion/extraction, Li-metal alloying/dealloying etc.

The capacity of the dendrimer-linked nitroxide cathode decreased gradually with charge/discharge cycles due to dissolution of active material into the electrolyte. The strategy to reduce the dissolution of DENDN-650 in organic electrolyte has been addressed and both the capacity and stability has been greatly improved.

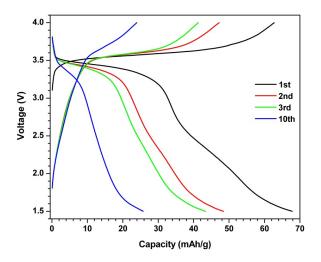


Fig. 2 Voltage *vs* specific charge-discharge capacity of DENDN-650 electrode cycled at 10 mA/g rate between 4.0 V and 1.5 V *vs* Li/Li⁺ in 3 M solution of LiPF₆ in 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) as the electrolyte.

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References:

[1] A. Reddy, S. Nagarajan, P. Chumyim, S.R. Gowda, P. Pradhan, S.R. Jadhav, M. Dubey, G. John, P.M. Ajayan, Lithium storage mechanisms in purpurin based organic lithium ion battery electrodes, *Sci. Rep.*, 2 (2012).

[2] T. Nokami, T. Matsuo, Y. Inatomi, N. Hojo, T.Tsukagoshi, H. Yoshizawa, A. Shimizu, H. Kuramoto, K. Komae, H. Tsuyama, J. Yoshida, Polymer-Bound Pyrene-4,5,9,10-tetraone for Fast-Charge and -Discharge Lithium-Ion Batteries with High Capacity, *J. Am. Chem. Soc.*, *134* (2012), 19694-19700.

[3] C.S. Winakski, S. Shortkroff, R.V. Mulkern, E. Schneider, G.M. Rosen, Magnetic Resonance Relaxivity of Dendrimer-Linked Nitroxides, Magn. Reson. Med., 48 (2002), 965-972.