π-Stacked Supramolecular Oligomers for Supercapacitors

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π-stacked supramolecules have been proposed by us as a new generation of energy storage materials with high capacity and long cycle life characteristics for use in proton batteries and supercapacitors. The authors will introduce two different kinds of novel electroactive supramolecules base on 1,5-diaminoanthraquinone (DAAQ) and cyclic indole trimer (CIT).

An electrooxidation gave a π-stacked supramoleculer oligomer of DAAQ (fig.1(a)) which was obtained as a thin film, exhibiting a charge density of 50 Ah kg^{-1} in 4 M H_2SO_4 aqueous solution[1]. Besides showing high specific capacity, the oligomeric DAAQ supramolecule maintained its crystalline structure by π-π interaction, and therefore showed reproducible redox responses over 20,000 cycles with little capacity loss of about 5% of the initial capacity density[2] (fig.2). Such an enhanced cycleability is caused by an isotropic expansion and shrinkage of the lattice during repetition of ion doping/undoping process.

We have also attempted to newly prepare π-stacked supramolecule consisted of cyclic indole trimer (CIT supramolecule (fig. 1(b))), which has higher redox potential (up to 1.0 V *vs.* Ag/AgCl) than the oligomeric DAAQ supramolecule and any other redox active organic materials.

Especially, the CIT supramolecule showed higher specific capacity (65 Ah kg^{-1}) and higher charge utilization (*ca*. 41% : the ratio of the obtained specific capacity to theoretical one (155 Ah kg^{-1})) as compared to the oligomeric DAAQ supramolecule (*ca*. 20%). In addition to its high specific capacity and high utilization, the CIT supramolecule exhibited excellent redox cycleability (about 100% of initial specific capacity after 25,000th cycle) (fig.2).

In this presentation, the electrochemical characteristics and conformation mechanism of the CIT supramolecule in acidic aqueous solution will be discussed.

References

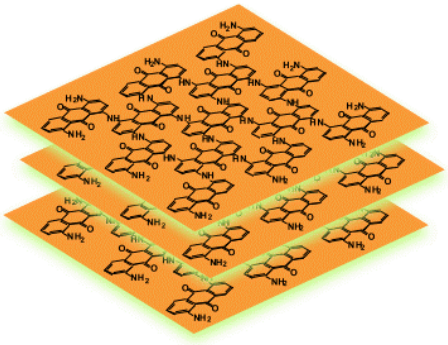
1) S. Suematsu and K. Naoi, *J. Power Sources,* **97-98,** 816 (2001).

2) K. Naoi, S. Suematsu, M. Hanada, and H. Takenouchi, *J. Electrochem. Soc*., in press.

3) T. Morimoto *et al*., *J. Power. Sources*, **60**, 239 (1996).

4) Uribe *et al*., *Proc. Electrochem. Soc*., **94-23**, 239 (1994).

(a) **DAAQ supramolecule**



(b) **CIT supramolecule**

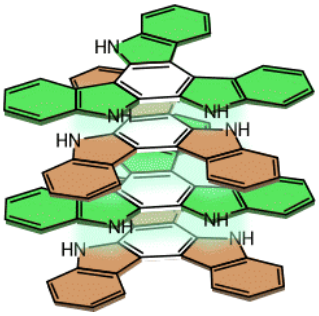


Fig.1 Schemeatic illustrations for the models of stacked supramolecules of (a) DAAQ and (b) CIT.

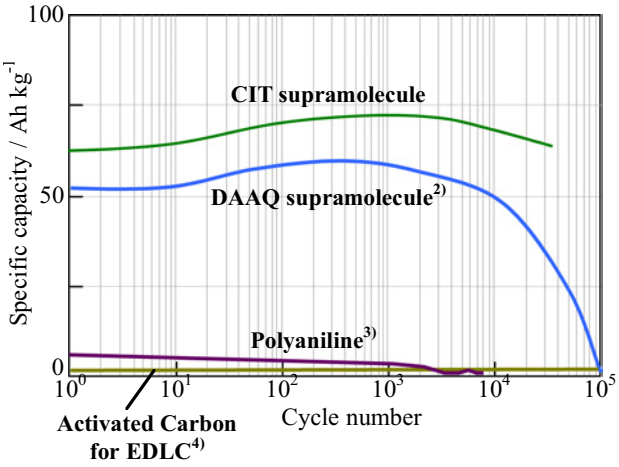


Fig.2 Specific capacity *vs.* cycle number for the DAAQ and CIT supramolecules as compared to the other redox active materials.