

## Organosulfur Supramolecules for Supercapacitors and Proton Batteries

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Sulfur-based materials have been in consideration as alternative high energy-density materials for lithium ion and lithium metal batteries. The materials generally undergoes energy exchange accompanying a reversible chemical formation / cleavage of disulfide bond (R-S-S-R / 2R-SH). There are two main types of materials which are featured in recent years as cathodes utilized in lithium secondary battery systems, viz., carbon sulfide compounds (Moltech Co.)<sup>1)</sup> and active sulfur (PolyPlus Co.)<sup>2)</sup> compounds. The capacity densities obtained for these are generally as high as 500~900 Ah kg<sup>-1</sup> per active cathode materials as compared with inorganic intercalation cathodes.

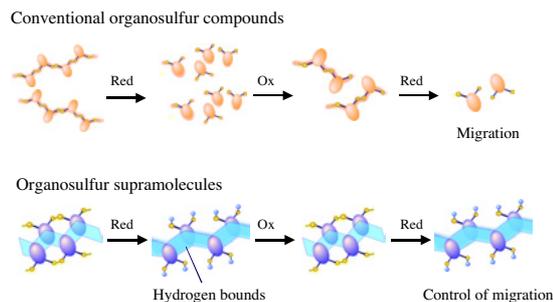
Yet, these compounds have two drawbacks in relation to the low rate constant at room temperature and low coulombic efficiency due to the migration of reduced species like monomers or dimers. To overcome these, we studied a series of supramolecules based on organosulfur monomers interconnected via hydrogen bonds. (Fig.1).

Among them, we have focused on 2-amino-4, 6-dimercaptopyrimidine (ADMP). The structural characteristics of a ribbon-form (Fig.2) of ADMPs are confirmed by spectroscopic techniques such as FT-NMR and FT-IR. Analysis by XRD and UV-vis spectroscopy supported the fact that they are stacked one another maintaining the ribbon forms when they were prepared in aqueous solution with low pH values (pH=1).

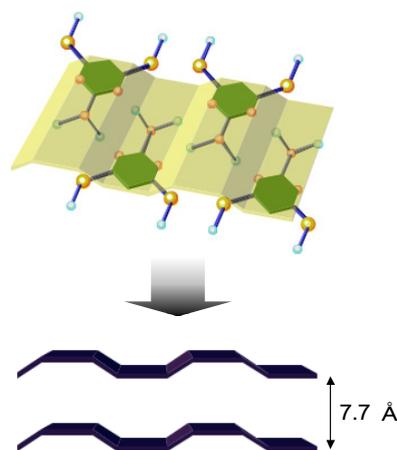
The ADMP supramolecule has shown high redox activity in acidic aqueous solution of 4M H<sub>2</sub>SO<sub>4</sub>, and delivered high capacity density (max. 112 Ah kg<sup>-1</sup> in 4M H<sub>2</sub>SO<sub>4</sub>). After cycling 700 times, the ADMP still maintained 50% of its initial capacity.

### References

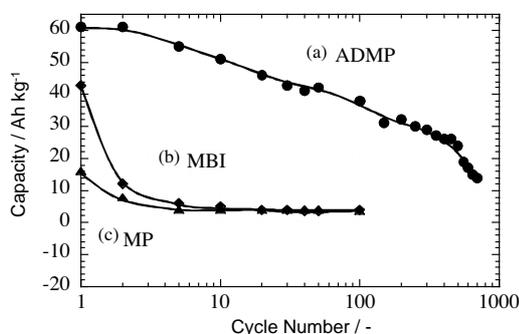
- 1) T. A. Skotheim *et al.*, U. S. Patent, 5, 460, 905 (1995).
- 2) M. Y. Chu *et al.*, U. S. Patent, 5, 523, 179 (1996).



**Fig. 1** Comparison of conventional organosulfur compounds to organosulfur supramolecules in the redox mechanism.



**Fig. 2** Schematic illustration for ribbon-like polymeric motif of ADMP supramolecule.



**Fig. 3** Plot of specific capacity vs. cycle number for (a)ADMP, (b)2-mercaptobenzimidazole(MBI), and (c)2-mercaptopyrimidine(MP).