

Supporting Information

3,6-Diphenyltetrazine as Cathode Active Material for Sodium Ion Batteries

Jun WATANABE,^a Masaki FURUSAWA,^{b,c} Kosuke NAKAMOTO^{b,c,§} Yuchao SUN,^{ad}
Masatoshi TASHIMA,^a Keiko YAMAOKA,^b Seiko FUJIWARA,^b Han Seul KIM,^{a,e}
Shigeto OKADA^{b,c,§*} and Ken ALBRECHT^{b,c,f,§*}

a. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-Koen Kasuga Fukuoka 816-8580, Japan

b. Institute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga-Koen Kasuga Fukuoka 816-8580, Japan

c. Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, 1-30 Goryohara Kyoto Nishikyo-ku Kyoto 615-8245, Japan.

d. School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

e. Graduate School of Nanofusion Technology, Pusan National University, Busandaehak-ro 63beon-gil, Jangjeon2(i)-dong, Geumjeong-gu, Busan, 46241, Republic of Korea

f. JST-PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.

*Corresponding Authors: s-okada@cm.kyushu-u.ac.jp (S. O.), albrecht@cm.kyushu-u.ac.jp (K. A.)

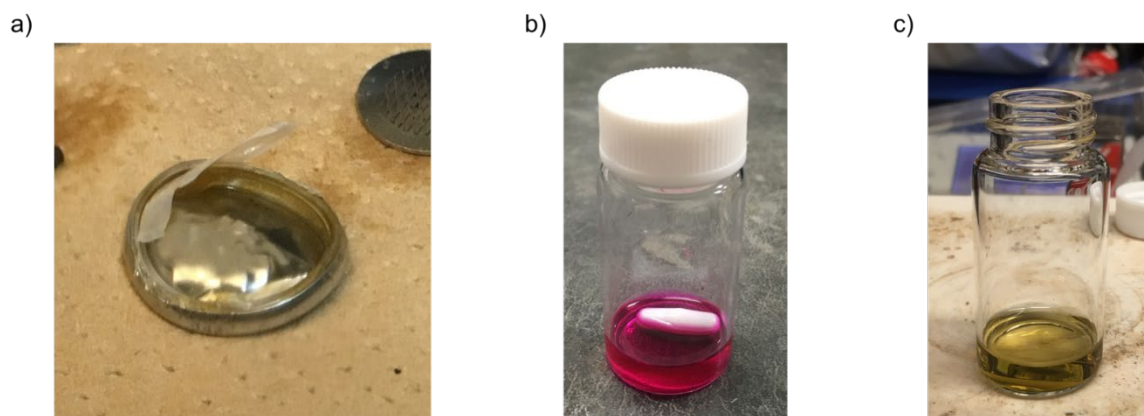


Figure S1.

a) Photograph of a dismantled battery cell after discharge-recharge measurements. The yellowish cloudy electrolyte can be seen at the edge of the cell. b) The THF solution of DPT just after adding sodium pieces. c) DPT THF solution after stirring for 3 h with sodium pieces and filtered. The characteristic color of the DPT changed to a similar color as that of the electrolyte after charging and discharging.

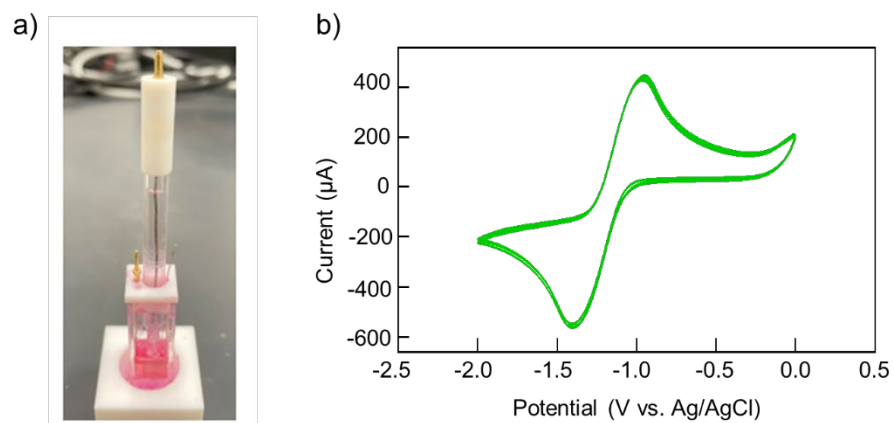


Figure S2.

a) Spectro electrochemistry setup and b) the cyclic voltammogram of DPT. The electrochemical measurement was carried out using a three-electrode configuration with an ALS Chi660 electrochemical ECstat 301. The working, counter, and reference electrodes were Pt mesh, Pt wire, and Ag/Ag⁺, respectively. The solvent was MeCN, the concentration of the sample was 0.1 mM, and the supporting electrolyte was 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆). The solution was purged with nitrogen before the measurements. The voltage scan rate was 0.05 V/s for the CV.

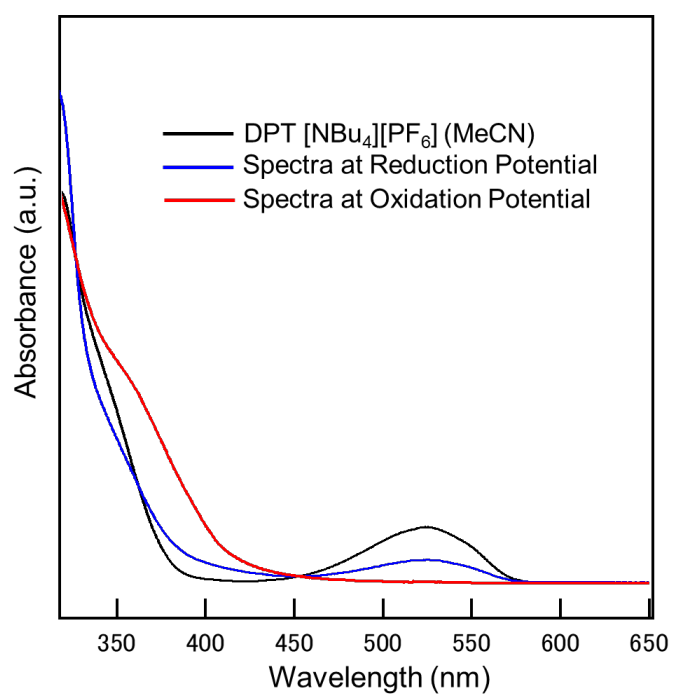


Figure S3.

UV-vis spectra of DPT in MeCN electrolyte (black), after bulk electrolysis (reduction at -1.4 V, 60 min, red), and bulk electrolysis (re-oxidation at -0.9 V, 60 min, blue).

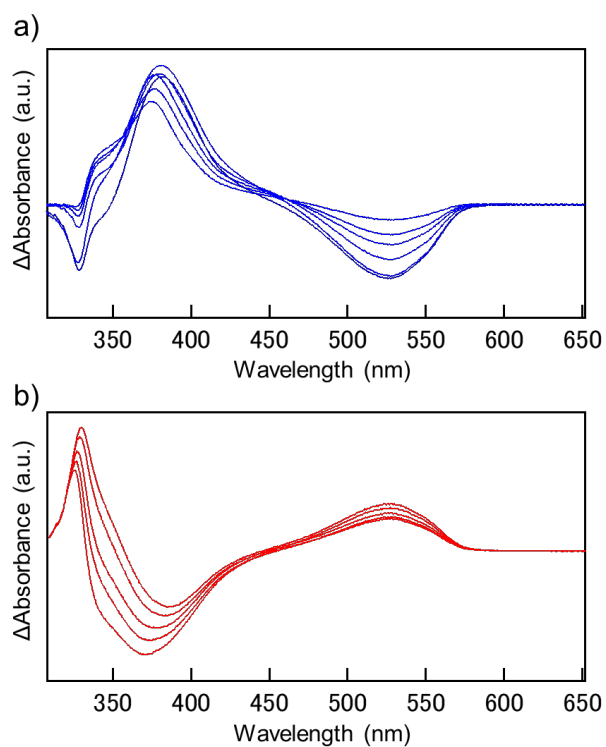


Figure S4.

Differential UV-vis spectra during the bulk electrolysis (measured every 3 min.). (a) reduction at -1.40 V. (b) oxidation at -0.93 V. Clear decrease of absorption at 540 nm of tetrazine and increase at 390 nm during reduction is observed.

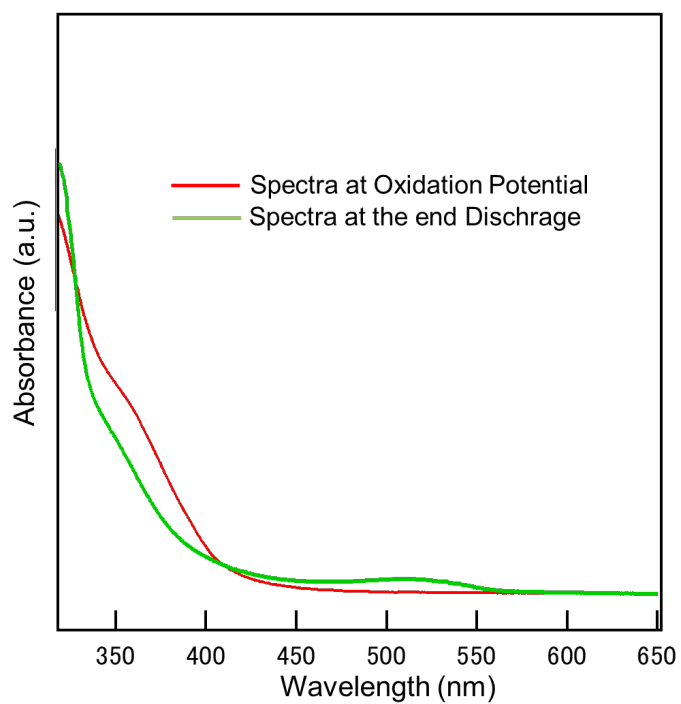


Figure S5.

UV-vis spectra of DPT in MeCN electrolyte at the reduction potential (red), and the electrolyte extracted from the dismantled cell after discharge was diluted with MeCN (green). This indicated the existence of neutral DPT and reduced DPT (anion) in the electrolyte after the charge/discharge cycle.

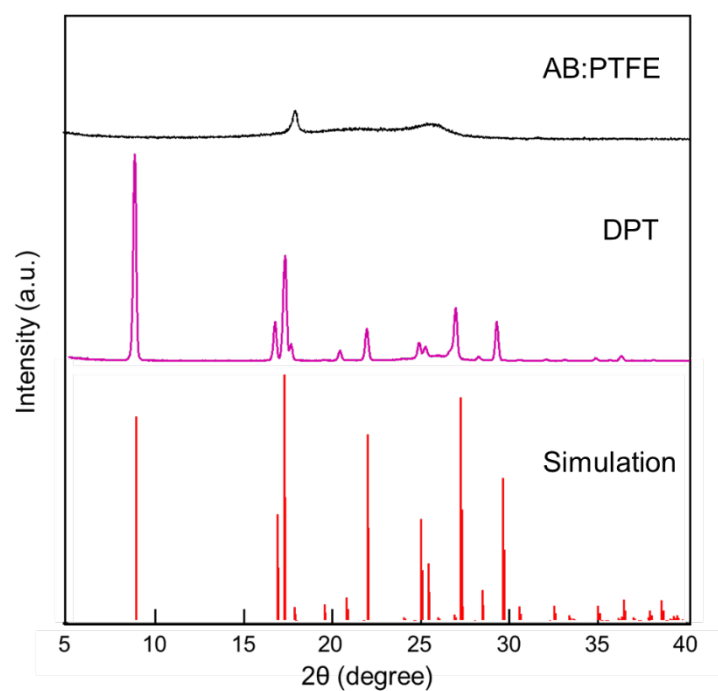


Figure S6.

XRD patterns of DPT, AB and PTFE mixed in 9:1 ratio by weight and simulated pattern¹ from previously reported Crystal information file. The peak of PTFE is at 17.0° and overlaps with that of DPT. In the ex situ XRD results, the vertical scale width was adjusted based on the peak of PTFE, whose height does not change during charging/discharging.

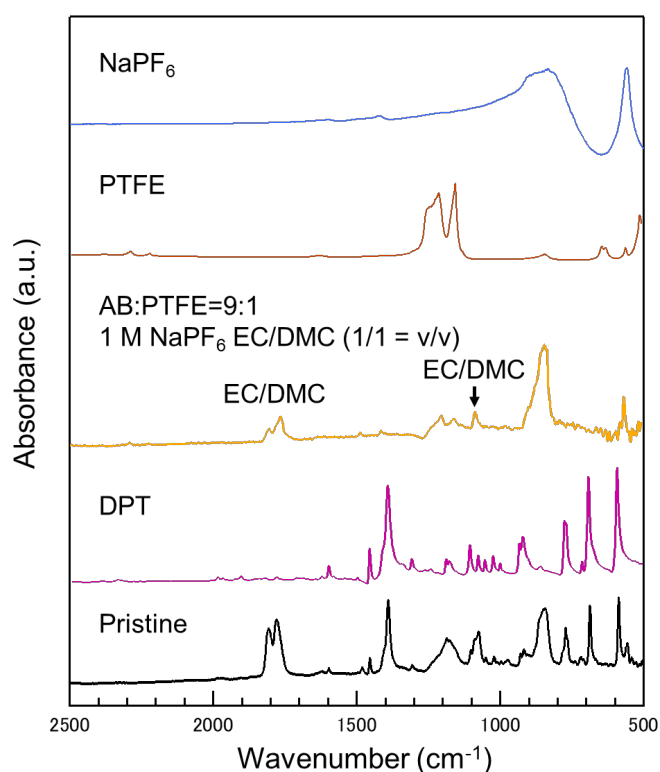


Figure S7.

FT-IR spectra measured under vacuum. NaPF_6 , PTFE, DPT, and a mixture of AB and PTFE in a 9:1 weight ratio impregnated with 1 M NaPF_6 EC/DMC (1/1 = v/v) overnight (vacuum). In this figure, the DPT peaks of interest are revealed by proving the peaks of the PTFE, NaPF_6 , and EC/DMC, whose peak intensities do not originally change during discharge-recharge. NaPF_6 has a sharp peak at 570 cm^{-1} and a broad peak at 850 cm^{-1} . PTFE has two characteristic peaks at 1160 cm^{-1} and 1220 cm^{-1} . For the pellet impregnated with 1 M NaPF_6 EC/DMC (1/1 = v/v) overnight after mixing AB and PTFE in a 9:1 weight ratio, peaks at 1090 cm^{-1} , 1780 cm^{-1} , and 1800 cm^{-1} were observed. From the above results, peaks at 850 cm^{-1} , 1090 cm^{-1} , 1780 cm^{-1} , and 1800 cm^{-1} are not originated by the active material (DPT) in the pellet. This means that the peak intensity depends on the drying condition of the pellet and not on the charge/discharge depth.