

Monitoring the Electrochemical Energy Storage Processes of an Organic Full Rechargeable Battery via *Operando* Raman Spectroscopy - A Mechanistic Study

Xiu-Mei Lin,^{*,†,‡} De-Yin Wu,^{*,§} Ping Gao,[†] Zhi Chen,^{||} Mario Ruben,^{||} Maximilian Fichtner^{*,†,||}

[†]Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), Helmholtzstr. 11, 89081 Ulm, Germany

[‡]Department of Physics, Xiamen University, 361005 Xiamen, China

[§]State Key Laboratory of Physical Chemistry of Solid Surfaces, iChEM, College of Chemistry and Chemical Engineering, Xiamen University, 361005 Xiamen, China

^{||}Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), P.O. Box 3640, 76021 Karlsruhe, Germany

*E-mail: xiu-mei.lin@xmu.edu.cn

dywu@xmu.edu.cn

m.fichtner@kit.edu

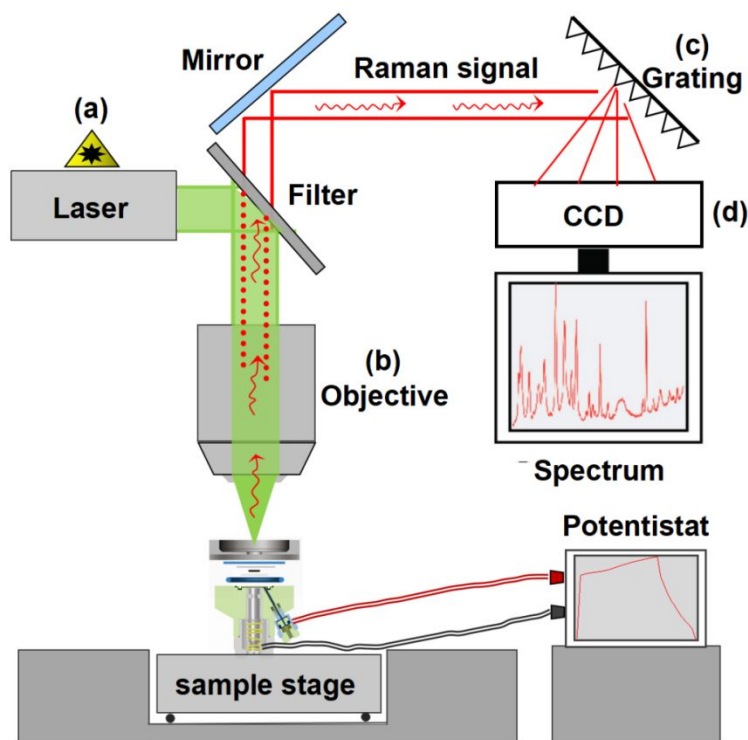


Figure. S1. Schematic illustration of the *operando* electrochemical Raman spectroscopy system.

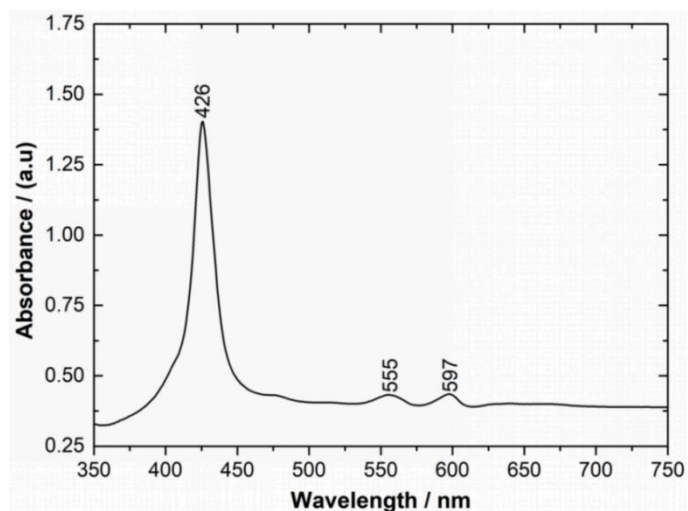


Figure. S2. UV-Vis adsorption spectrum of CuDEPP.

Calculation of theoretical capacity of CuDEPP:

Formula of CuDEPP: $C_{36}H_{20}CuN_4$; Formula weight of CuDEPP: 572.14 g/mol

$$\text{Theoretical capacity} = nF/M = 2 \times 96485 \times 1000 / (572.14 \times 3600) = 93.69 \text{ mA h g}^{-1}$$

n: the number of transfer electrons; F: Faraday constant (96485 C); M: Formula weight

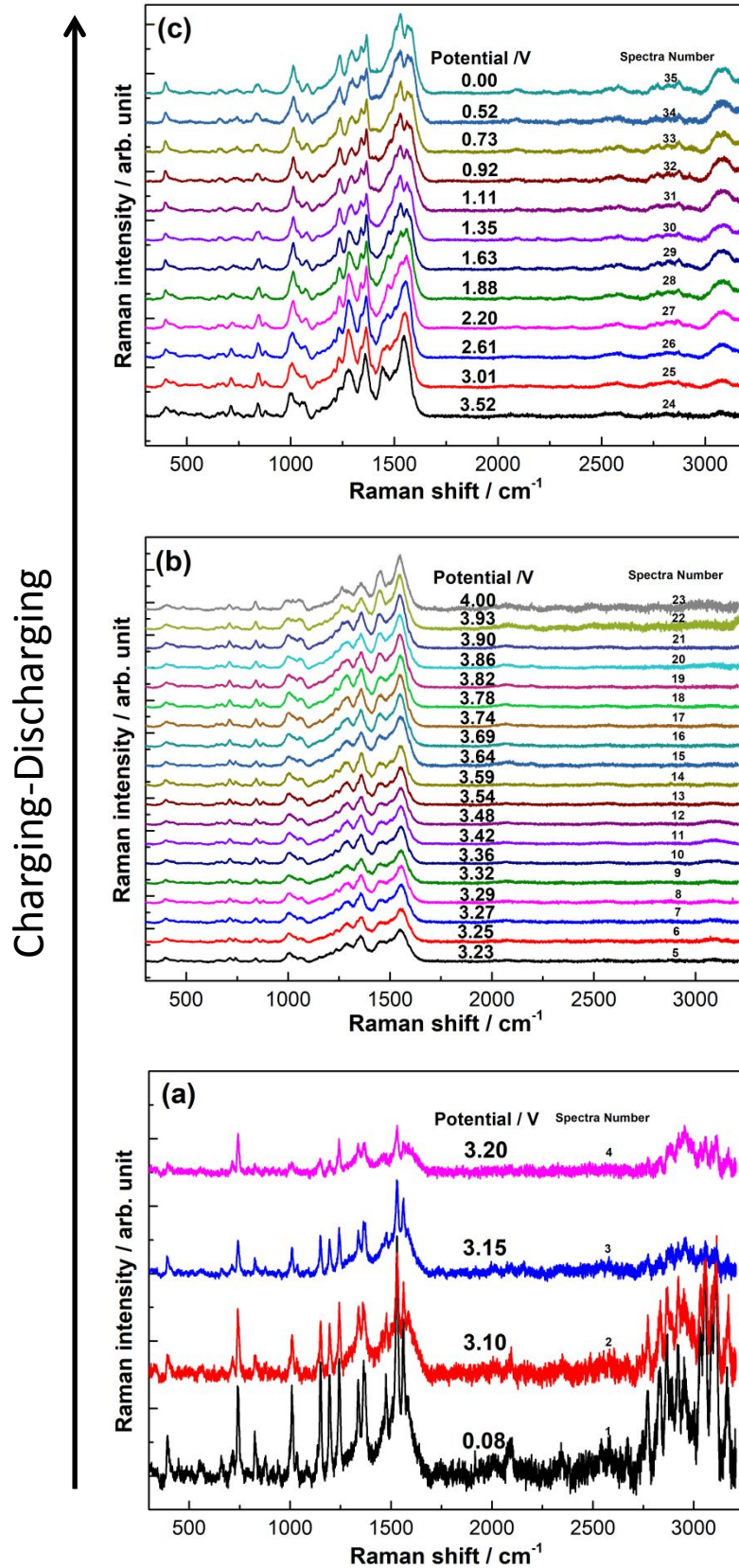


Figure. S3. (a)-(c). Series of Raman spectra of the CuDEPP anode during initial charge-discharge cycling with a full spectral range from 300 cm⁻¹ to 3200 cm⁻¹ and with the corresponding potential on each spectrum.

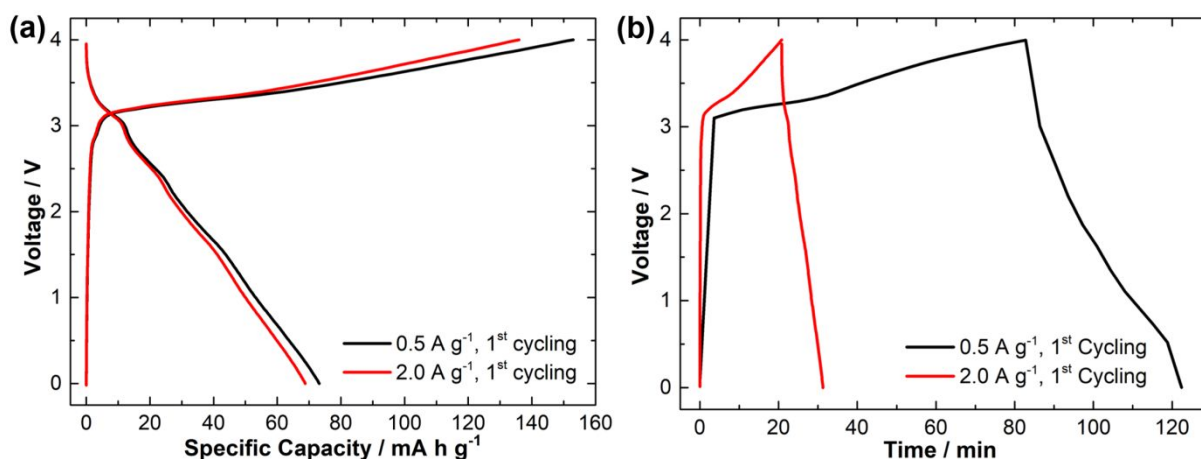


Figure. S4. (a) Galvanostatic charge-discharge profiles; (b) “Voltage vs cycling time” curves of the CuDEPP / PP14TFSI / Graphite organic full rechargeable battery for the 1st cycle at specific current of 0.5 A g⁻¹ and 2.0 A g⁻¹ respectively.

Table S1: Band assignment of the Raman spectra of CuDEPP¹⁻⁷

Frequency / cm ⁻¹		
Observed	References	Assignment
3164, 3110, 3089, 3057, 3035, 2957, 2925, 2865, 2833, 2769	2700 - 3200	vCH
2090, 2070, 2090	2000 -2200	vC≡C
1557, 1525, 1546, 1557, 1525	1564, 1531	vC _{Pr} C _m
1471, 1447, 1471	1477	vC _{Pr} C _{Pr}
1371, 1337, 1356, 1371, 1337	1372, 1340	vC _{Pr} C _{Pr}
1287	1290	vC _{Pr} N
1244	1241	vC _{Ph} C _m
1081, 1062, 1081	1080	δC _{Pr} H
1010	1006	δC _{Ph} C _{Ph} C _{Ph}
876	884	δC _{Ph} C _{Ph} C _{Ph}
824, 845	849	δC _{Pr} C _m C _{Pr}
739	742	δC _{Pr} C _{Pr} C _{Pr}
712	696	δC _{Ph} C _{Ph} C _{Ph}
395	410	vCuN

C_{Pr}: pyrrole carbons; C_{Ph}: phenyl carbons; C_m: methine bridge carbons; v: stretching; δ: in-plane deformation.

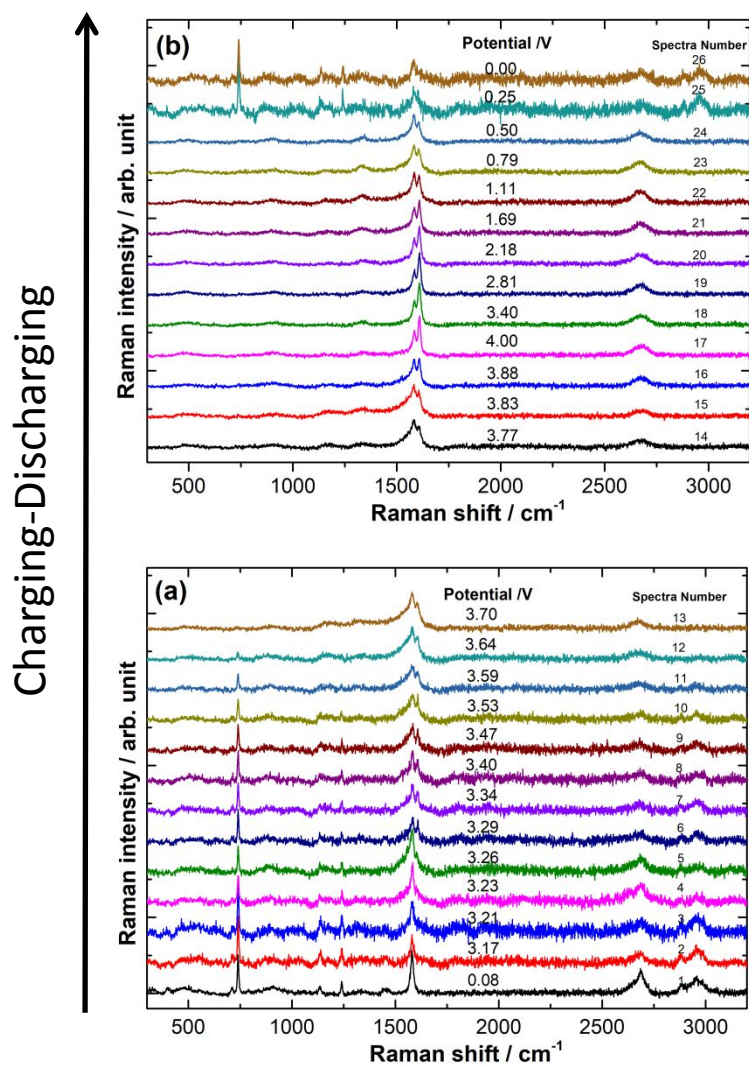


Figure S5. (a), (b). Series of Raman spectra of the graphite cathode during initial charge-discharge cycling with a full spectral range from 300 cm⁻¹ to 3200 cm⁻¹ and with the corresponding potential on each spectrum.

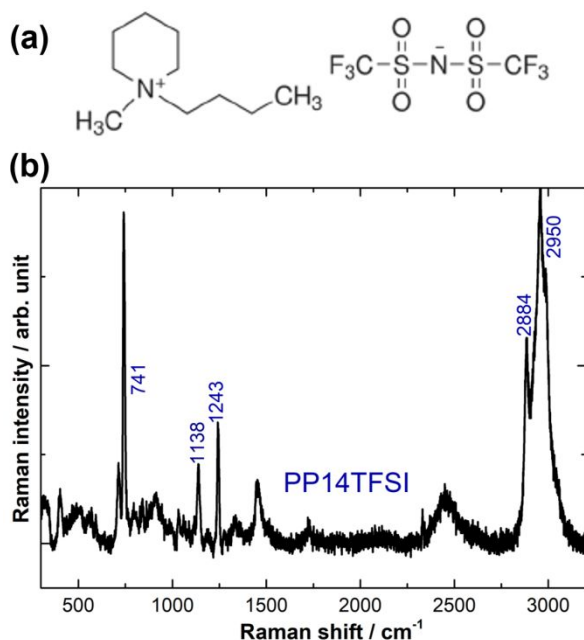


Figure S6. Molecular structure (a) and Raman spectrum (b) of PP14TFSI ionic liquid electrolyte.

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