and B (III)→(II), respectively, occurs primarily between 0 and -1 V. However, the battery behavior involving oxidation from Mn(II) to Mn(III) and then to Mn(IV), i.e., B (II)→(III) and B (III)→(IV), respectively, concurrently occurs with PC (IV)-(III) from -0.3 to 1 V. The figure also illustrates that the battery behavior provides a substantial amount of charge-storage capacity in addition to pseudocapacitance at low scan rates. This study suggests a new strategy to design and develop new electrochemical electrode materials for more efficient energy storage and wider applications.

Reference

Yu-Ting Weng, Hsiao-An Pan, Rung-Chuan Lee, Tzu-Yang Huang, Yun Chu, Jyh-Fu Lee, Hwo-Shuenn Sheu and Nae-Lih Wu, (2015). Spatially Confined MnO_2 Nanostructure Enabling Consecutive Reversible Charge Transfer from Mn(IV) to Mn(II) in Mixed Pseudocapacitor-Battery Electrode. *Advanced Energy Materials*, 5, 1500772. DOI: 10.1002/aenm.201500772.

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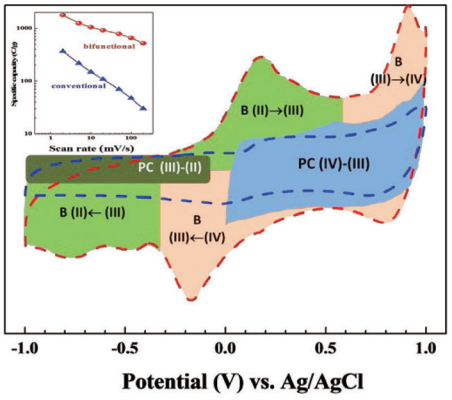

Figure 2. Schematic of the various charge-storage mechanisms as a function of potential; B: battery behavior; PC: pseudocapacitance; (IV), (III) and (II): Mn ions with a valence of 4, 3 and 2, respectively. The inset compares the charge-storage capacities between the bifunctional MnO_2_SiO_2 composite electrode (red) and a conventional MnO_2 electrode (blue).

Post lithium-ion batteries: lithium-sulfur batteries

Probing the discharge and charge mechanism of lithium-sulfur batteries

The ever-rising demand for portable power sources has prompted a renewed interest in next-generation energy storage systems, including batteries, fuel cells and electrochemical capacitors. The applications of these energy storage devices range from consumer electronics to next-generation electric vehicles. Among the various energy storage technologies, batteries are by far the most successful products in the consumer market. Although Li-ion batteries (theoretical specific energy of C/$LiCoO_2$ is ~387 Wh kg^{-1}) still dominate the portable electronic device market, their capacity cannot reach the requirements of batteries for electric vehicles. Next-generation Li batteries, such as Li-S batteries, have attracted attention recently, mainly due to their low cost and high theoretical specific energy of ~2567 Wh kg^{-1}. However, many problems associated with the battery performance, such as dendrite formation at the Li anode and dissolution of intermediates from the S/C cathode, still limit the practical application of Li-S batteries.

To overcome these technical challenges regarding Li-S batteries, a detailed understanding of the discharge/charge mechanism is needed, as all the electrochemical reactions occurring on the cathode and anode are based on the fundamentals of electrochem-

ical thermodynamics and kinetics. Hence, we developed *operando* Raman/FT-IR/UV-Vis spectroscopy to examine the electrochemical reactions in the electrolyte and at the electrolyte-electrode interface under operating conditions together with real-time analysis of the reaction products. During the discharge process, *in situ* Raman spectroscopy obtained from the sulfur-carbon cathode showed that long-chain polysulfides (S_8^{2-}) were formed via S_8 ring opening in the first reduction process and that short-chain polysulfides, such as S_4^{2-}, S_4^{-}, $S_3^{\bullet-}$, and $S_2O_4^{2-}$, were observed with continued discharge in the second reduction process. All the formations of these intermediate species are reversible during the charge process.

These *operando* techniques enable us to study the formation of intermediate species, the formation/decomposition rate (kinetics) and the interaction between intermediate species and additives during cycling. The decomposition of the electrolyte on anode and cathode surfaces was observed using *operando* FT-IR spectroscopy. Performing *operando* Raman/FT-IR/UV-Vis spectroscopy with different spectral regions provides complementary information for the mechanismon the molecular level. Based on these findings, novel materials and electrolytes can be designed to achieve better performance.

Reference

Heng-Liang Wu, Minjeong Shin, Yao-Min Liu, Kimberly A. See, and Andrew A. Gewirth, (2017). Thiol-based electrolyte additives for high-performance lithium-sulfur batteries. *Nano Energy*, 32, 50-58. https://doi.org/10.1016/j.nanoen.2016.12.015

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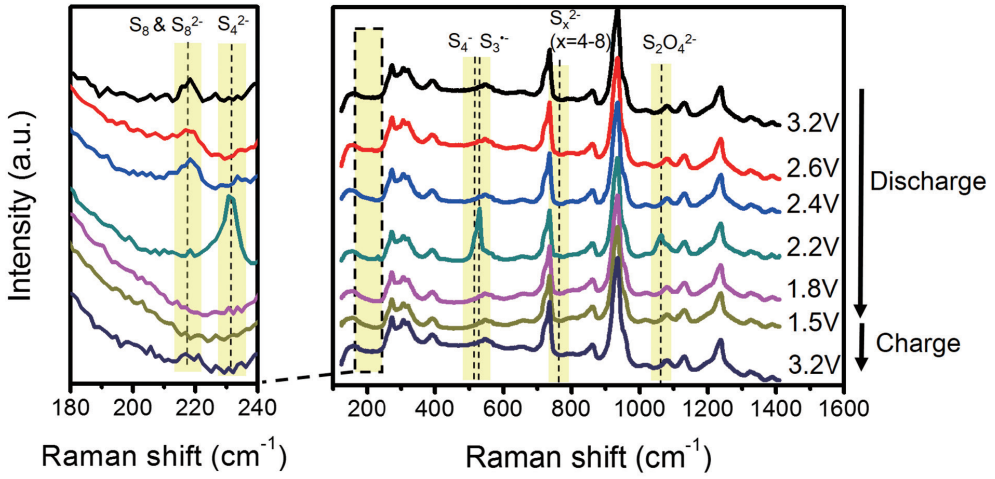

Figure 1. *In situ* Raman spectra of the sulfur-carbon cathode shown at representative potentials during discharge from 3.2 to 1.5 V and after recharging to 3.2 V

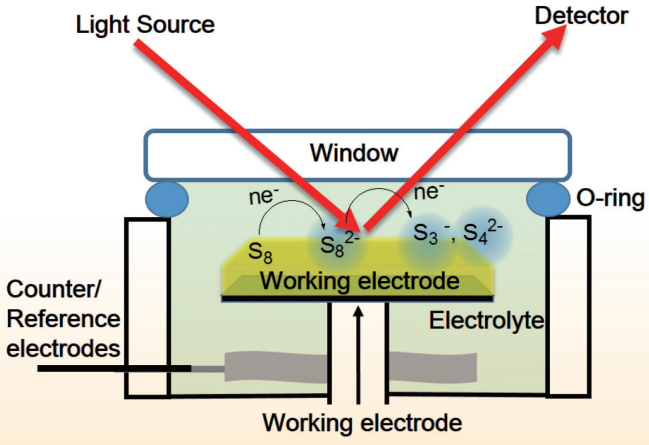

Figure 2. Illustration of the *operando* Raman/FT-IR/UV-Vis measurements