ATR-IR *operando* spectroscopy as a powerful tool for probing electrochemical reactions in organic cathode materials

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Li-ion batteries are a predominant battery technology on the battery market, but given the increasing demands for cheaper and more sustainable materials, different alternatives are actively explored (Li-S, Li-O_2, Na-ion, metal-organic batteries). Among those organic materials are especially interesting given the fact that they can be used with different counter ions (Li, Na, Mg, K). Although some of these materials show stable long-term cycling, electrochemical mechanisms in organic materials are rarely investigated. Main reasons are lack of suitable analytical techniques that would allow *operando* characterization of the organic cathode materials and fast degradation of *ex-situ* samples coupled with their troublesome handling. Thus, development of new characterization methods is needed for further progress of organic materials.

Herein, we develop a new, simple *operando* ATR-IR characterization method of organic materials in a modified pouch cell with Si wafer window. Si window enables us continuous measurements of ATR-IR spectra on cathode composite, while subtractive normalization allows visualization of all IR bands in the composite that are changing during electrochemical characterization.

We use *operando* ATR-IR to study electrochemical mechanism of poly (anthraquinonyl sulfide) (PAQS) in Li- and Mg-organic battery systems. The reduction of carbonyl bond is confirmed in both systems upon the electrochemical reduction. Good reversibility in Li and Mg system confirms applicability of PAQS as a cheap, versatile and sustainable cathode material. Results obtained by operando ATR-IR are supported by synthesis of model compounds and DFT calculations of theoretical IR spectra.

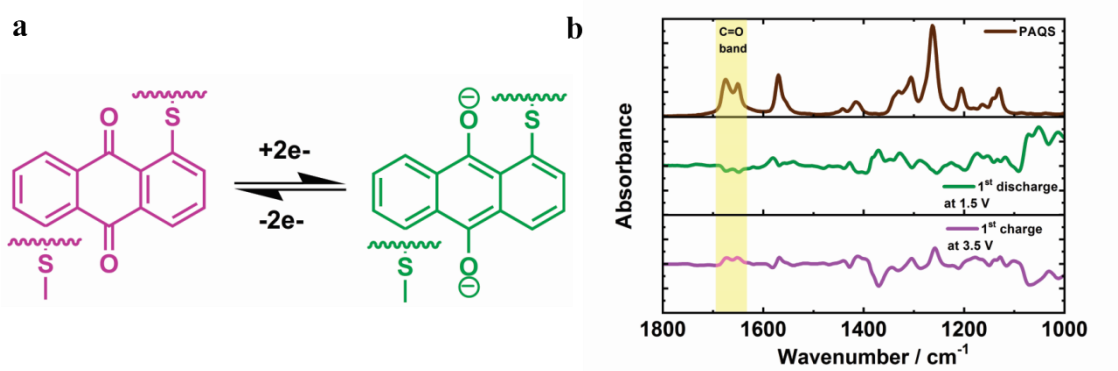

Figure 1: a) Proposed electrochemical mechanism of PAQS. b) IR spectra of PAQS (brown), differential spectra of PAQS cathode in first discharge (green) and charge (purple) of Li-PAQS battery.

References:

[1] A. Vizintin, J. Bitenc, A. Kopač Lautar, K. Pirnat, J. Grdadolnik, J. Stare, A. Randon-Vitanova, R. Dominko, Nat. Commun. Under review.