

Developing *Operando* Cells for Confocal Raman Spectroelectrochemistry

by Gabriel G. Rodríguez-Calero

The electrification of transportation and the need to store energy from renewable, but intermittent sources, has generated a great deal of interest in the study of electrode materials for electrochemical energy storage technologies.¹ It is not sufficient to study materials *in situ* because additional system components can give rise to deviations of the electrochemical reactions from the expected performance. In most cases, the interactions of the complete system are often underestimated. However, it is important to understand these complex interactions of the components of the system if we expect to incorporate new materials into traditional battery configurations and expect them to work as intended. Conducting polymers represent attractive materials for electrochemical energy storage technologies.² Their electrochemical reactions are well understood and have been studied by Raman spectroelectrochemistry.³ Even though these model systems (*i.e.*, *in situ* experiments) offer information about the changes undergone by the electrode during electrochemical cycling, factors such as film thickness, electrochemical charging/

discharging rate (C-rate), and cell geometry are different in real operating conditions. To better understand how these factors affect the electrochemical reactions of the electrode material, we have developed an electrochemical cell (Fig. 1) that contains Mylar windows by which we can measure Raman spectra of electrode materials while the cell is in *operando* conditions.

As a case study we chose poly-3,4-ethylenedioxythiophene (PEDOT); a conducting polymer film electropolymerized on current collectors. The current collector employed was gold-coated aluminum foil. We proceeded to assemble a 2 electrode cell, similar to a coin cell, in which the negative electrode was Li metal, the electrolyte was lithium hexafluorophosphate in propylene carbonate, and a polymer separator, Celgard, was employed. Electrochemical cycling at 1 mV/s for this half cell (Fig. 2c) was performed and Raman spectra were collected at 2.5 V and 4.2 V vs Li/Li+ (Fig. 2a and 2b, respectively). The reaction scheme is presented in the inset to Fig. 2c.

The Raman spectroelectrochemistry in the *operando* cell exhibits the typical Raman spectrum observed in *in situ* experiments.

When the polymer is in the neutral undoped state, sharper peaks for the Raman shifts around 1300 cm^{-1} can be observed. The peaks are then broader when the polymer is electrochemically oxidized from the neutral to the highly doped cationic state. The change is attributed to the quinoid-type bonding that the polymer undergoes when oxidized.

In this particular case the electrode material was not found to be influenced by the presence of Li metal, the Celgard separator, or the overall cell configuration. The film thickness appears to cause some resistive behavior as evidenced by the slope in the LSV. However, there are no indications in the Raman spectra in the region studied that the polymer is being affected by the other components of the system. In conclusion, We have effectively fabricated an *operando* Raman spectroelectrochemical cell and effectively studied a PEDOT electrode material during electrochemical cycling. Most importantly We found that the other components of the system do not affect the electrochemical reactions of PEDOT as evidenced by the similarities between the *in situ* and *operando* experiments.

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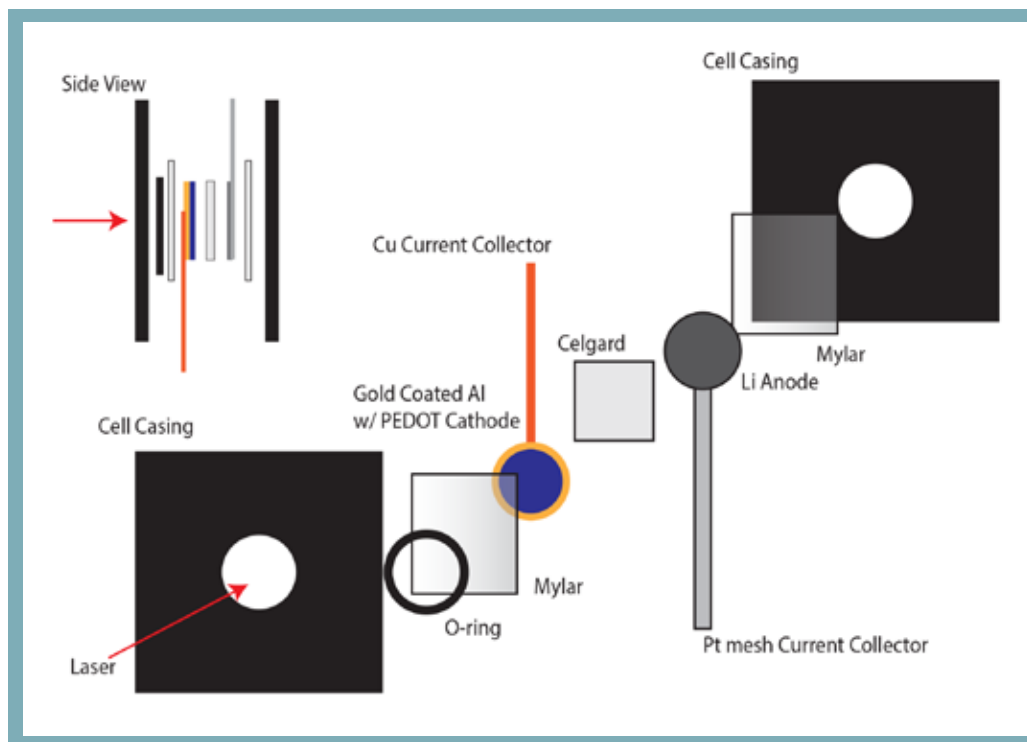


FIG. 1. Schematic of operando Raman spectroelectrochemical cell.

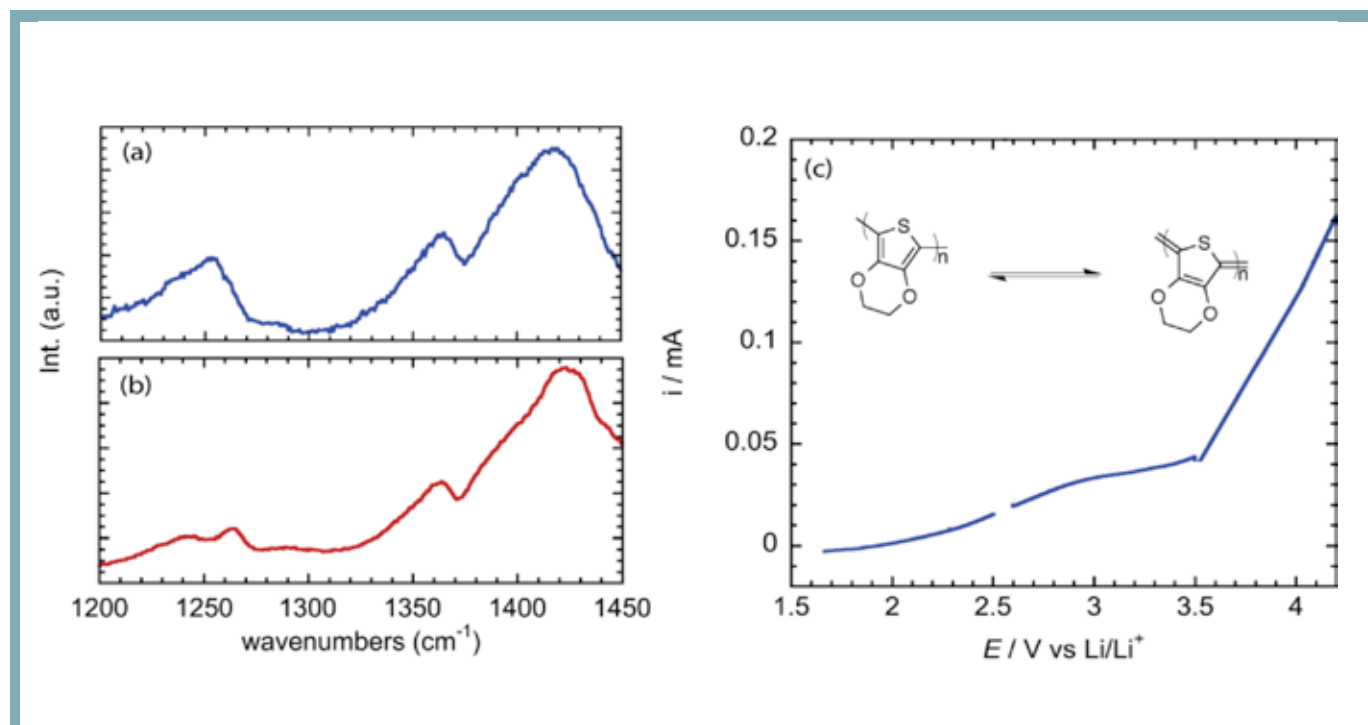


FIG. 2. Raman spectra of a PEDOT film on a gold coated aluminum current collector obtained at (a) 2.5 V vs Li/Li⁺ and (b) 4.5 V vs Li/Li⁺. (c) LSV of a PEDOT film on a gold coated aluminum current collector in 1 M LiPF₆/PC electrolyte using a 2 electrode configuration with a sweep rate of 1mV/s.

Acknowledgments

I would like to thank ECS for honoring me with the Colin Garfield Fink Summer Fellowship, and my advisor, Prof. Héctor D. Abruña, for his guidance and support on the work presented herein. ■

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