

## Methods for Enhancing the Flowable Electrode Capacitance in the Electrochemical Flow Capacitor

K.B. Hatzell<sup>1</sup>, M. Beidaghi<sup>1</sup>, M. Boota<sup>1,2</sup>, C.R. Dennison<sup>1,2</sup>, E.C. Kumbur<sup>2</sup>, Y. Gogotsi<sup>2</sup>

<sup>1</sup>A.J. Drexel Nanotechnology Institute,  
Department of Material Science and Engineering  
<sup>2</sup>Electrochemical Energy Systems Laboratory,  
Department of Mechanical Engineering and Mechanics

Drexel University, Philadelphia, PA 19104

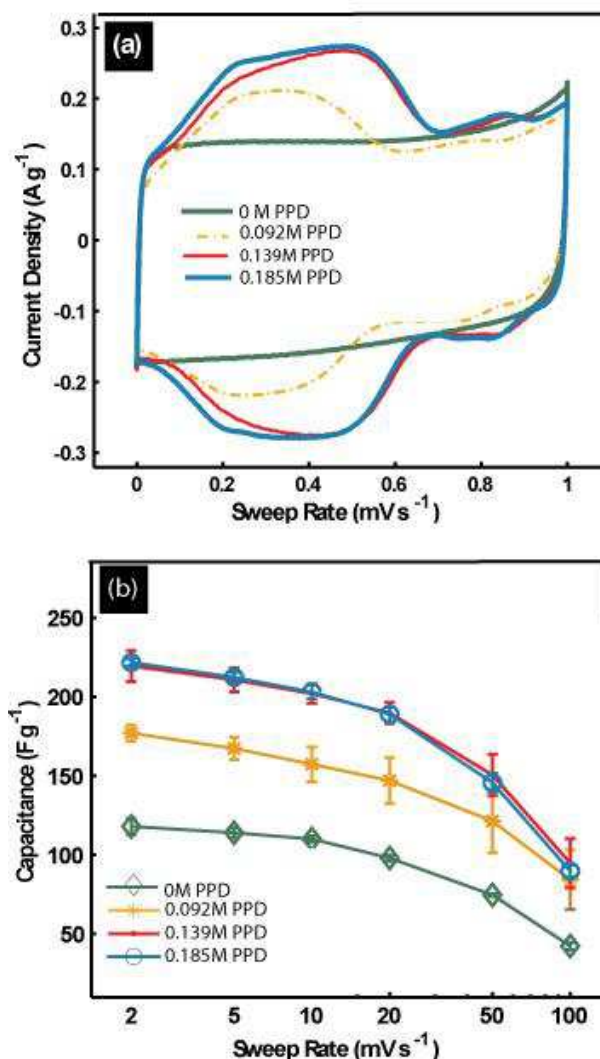
\*Corresponding Author: [gogotsi@drexel.edu](mailto:gogotsi@drexel.edu),  
[eck32@drexel.edu](mailto:eck32@drexel.edu)

Grid energy storage has emerged as one of the key challenges limiting grid resiliency and impeding the full integration of intermittent renewable energy technologies. A novel technology that can address this issue is the electrochemical flow capacitor (EFC)[1,2,3]. The primary difference between traditional supercapacitors and the EFC is that the EFC utilizes a flowable electrode for capacitive energy storage. The electrostatic nature of this charge storage mechanism allows for fast charging and discharging, which allows the EFC to be tailored to specific grid applications such as voltage and frequency regulation where short response times are needed [4]. The EFC concept benefits from the advantages of both supercapacitors and flow batteries in that it is capable of rapid charging/discharging, has a long cycle lifetime, and enables energy storage and power to be decoupled and optimized for the desired application.

The EFC's flowable electrode is comprised of active material (spherical activated carbon), electrolyte (2M KOH), and a conductive additive (carbon black). Thus, similar to traditional supercapacitors, the EFC is limited in terms of energy density, when compared to batteries. To address this limitation we incorporated redox mediators into the flowable electrode to enhance the capacitance. Redox-mediated electrolytes provide an additional charge storage mechanism (faradaic) which ultimately increases the capacitance and ionic conductivity while simultaneously making the flowable electrode pseudocapacitive in nature[5].

We have prepared carbon-electrolyte slurries with different concentrations of p-phenylenediamine (PPD), a redox mediator, and examined its performance in a static configuration. An increased capacitance on the order of 86% when compared with KOH electrolytes, and a 130% increase when compared to previously reported neutral electrolyte slurries was observed [1,3]. A concentration of 0.139 M of PPD in 2 Mol KOH yielded the greatest capacitances in both cyclic voltammetry (CV) and galvanostatic cycling experiments. The slurries with the redox mediators demonstrate redox peaks in the CV experiments, which diverge from the quasi-rectangular shape typical of an ideal double layer capacitor (**Fig. 1a**). The rate performance of the redox-mediated slurry shows similar capacity retention to the slurries without the redox mediator indicating that the PPD does not hinder transport (**Fig. 1b**). The high performance is attributed to the addition proton coupled electron transfer (PCET) at the active material interface as p-phenylenediamine undergoes a two-proton/two-electron reduction and oxidation reaction.

We have also investigated the effects of pore size distribution and ammonization of the carbon surface as possible methods to increase the capacitance of the active material in the flowable electrode.



**Figure 1.** (a) Cyclic voltammetry performance for different concentration of P-phenylenediamine (PPD) in a 2M KOH electrolyte based flowable electrode at  $2 \text{ mV s}^{-1}$ . (b) Rate performance for the pseudocapacitive electrode at varying concentrations of PPD.

### References:

1. Presser, V., Dennison, C. R., Campos, J., Knehr, K. W., Kumbur, E. C., & Gogotsi, Y. The Electrochemical Flow Capacitor: A New Concept for Rapid Energy Storage and Recovery. *Advanced Energy Materials*, **2012** 2(7), 895-902.
2. Gogotsi, Y., Presser, V., and Kumbur, E. C., "The electrochemical flow capacitors," Patent Application, PCT/US2012/024960, **2012**.
3. Campos, J. W., Beidaghi, M., Hatzell, K. B., Dennison, C. R., Musci, B., Presser, V., Kumbur, E. C. Gogotsi, Y. Investigation of Carbon Materials for Use as a Flowable Electrode in Electrochemical Flow Capacitors. *Electrochimica Acta*, **2013** (98) 123-130.
4. Dunn, Bruce, Haresh Kamath, and Jean-Marie Tarascon. "Electrical energy storage for the grid: A battery of choices." *Science* **2011** 334.6058: 928-935.
5. Hatzell, K.B., Beidaghi, M., Campos, J. W., Dennison, C. R., Musci, B., Presser, V., Kumbur, E. C. Gogotsi, Y. A High Performance Pseudocapacitive Flowable Electrode for the Electrochemical Flow Capacitor. *Electrochimica Acta*, **Submitted**.