Enhanced Electrochemical Supercapacitors
Integrating with Polythiophene
Using Oxidative Chemical Vapor Deposition
Siham Nejati, Chau Tran, Thomas E. Minford, Vibha Kalra and Kenneth K. S. Lau
Department of Chemical and Biological Engineering
Drexel University
3141 Chestnut Street, Philadelphia, PA 19104

Oxidative chemical vapor deposition (oCVD) represents a novel CVD method for producing polymer thin films in a one-step polymerization and deposition process. Using oCVD, we can synthesize polymers without any need for solvents. Here, we have utilized oCVD to create conjugated thiophene polymers directly within the complex structure of carbon nanofiber-based electrochemical supercapacitor electrodes with the aim of enhancing capacitance and bridging the technology gap between current lithium batteries and electrolytic capacitors.

Polythiophene among conjugated polymers is known to have high charge storage capacity, which comes from their ability to undergo p- and n-doping. The application of chemically synthesized polythiophenes in electrochemical supercapacitors has been demonstrated previously and this polymer has been introduced as a good candidate to be used in a composite with activated carbon. The composite made from polythiophene has shown high energy density and high capacitance, however, the synthetic pathway to integrate polythiophene mostly relied on wet chemical and electrochemical methods, which owing to the lack of polymer solubility and the need for conducting electrodes limit the utility of current liquid synthesis techniques. Our approach of using a scalable oCVD synthesis that eliminates the need for a liquid solvent and overcomes liquid synthesis challenges therefore proves valuable.

Here, we show that polythiophene can be directly synthesized and integrated by oCVD in different nanostructures to achieve enhanced pseudocapacitance above what is possible with the bare nanostructures. As seen in Figure 1a, the polymer is tightly integrated within a high surface area (55 m²/g) mesoporous network of titanium dioxide nanoparticles, which by itself has very minimal capacitance in 1 M tetraethylammonium tetrafluoroborate (TEABF₄). After polymer integration, the specific capacitance of the electrode is enhanced up to 70 F/g. The use of the titania network helps us to understand more carefully the role of the polythiophene alone within a nanostructured material. We have realized from the cyclic voltammogram of the samples that the charge trapping take place more significantly as the amount of mass within the matrix increases which consequentially results in reduced capacitance.

To further benefit from the charge storage capability of the polymer, the oCVD polymer coating was conducted on high surface area activated carbon and meso-porous carbon nanofiber that possess high electrochemical double layer capacitance. Meso-porous carbon nanofibers were fabricated via electrospinning, which is a simple fiber formation technique that uses strong electric field to thin a polymer solution jet forming nanoscale fibers. Figure 2 shows the bare mesoporous carbon nanofiber and fiber coated with polythiophene. The specific capacitance measured to be significantly enhanced from 80 F/g to 130 F/g in 1 M TEABF₄ when measured using galvanostatic charge-discharge at 1.4 mA/cm². Cyclic voltammetry of the uncoated and polythiophene integrated activated carbon was also performed on symmetric cells in a sandwich configuration using 1 M TEABF₄ in acetonitrile as the electrolyte and the capacitance of the cells was measured by integrating the voltammogram under reverse sweep. As shown in Figure 3, the specific capacitance of the polymer integrated activated carbon has been significantly increased from the bare electrode.

Interestingly, we have observed that the specific capacitance of the polymer integrated cell goes through an optimum as a function of ratio of the polymer to matrix weight when we varied the amount of polymer coating within the electrode simply by changing the amount of deposition time during oCVD, see Figure 4. This suggests that the polymer plays a critical role at the polymer-electrode interface. At very low thicknesses, an increase in the amount of the polymer naturally increases the polymer contribution to the overall capacitance. However, as thicknesses become too great, there is a possibility of transport limitations and also charge trapping that prevents the entire polymer to be involved in Faradic reactions for contributing pseudocapacitance.

References: