Electroactive Polymers as Battery Electrodes

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ABSTRACT

Plastic power, or energy storage platforms primarily consisting of polymers, offers opportunities never before available in current state-of-the-art prismatic or coin cells, such as flexible, structural, or stretchable energy storage. Electroactive polymers, a class of polymers that undergoes reversible reduction and oxidation, are currently explored as electrodes in batteries and electrochemical capacitors. Used alone or as part of a hybrid electrode, electroactive polymers are rapidly growing in interest due to their redox activity, conductivity, synthetic versatility, and mechanical properties. We will first introduce how electroactive polymers operate, their specific challenges, and latest advances specifically in batteries. Then, we will highlight spray-on polyaniline nanofiber-graphene based cathodes evaluated against lithium metal anodes. Finally, we will also present highly flexible and mechanically tough V_2O_5 hybrid electrodes, enabled by an electroactive block copolymer.

Keywords: electroactive polymer, batteries, cathode, conductivity

1 INTRODUCTION

Electroactive polymers are increasingly gaining interest for their redox activity and electronic properties, finding applications as battery or electrochemical capacitor electrodes or else as electroactive binders.[1, 2] Generally speaking, polymers uniquely offer mechanical flexibility, stretchability, and toughness not usually found in conventional metal oxide battery electrodes. They may also be solution processing such as spraying. Typical electroactive polymers include polyanilines, polythiophenes, and organic radical polymers.

Several key challenges for electroactive polymers include doping level or capacity and electrochemical stability. Many conjugated polymers achieve only a fraction of their theoretical capacity because of a limited doping level with higher doping levels leading to chemical degradation. Further, as electroactive polymers are incorporated into hybrid electrodes, they may interact in unexpected (either synergetic or not) with the other electrode material. These challenges motivate us to investigate the nature of electroactive polymers in terms of doping and stability, spray processing, as well as their role in hybrid electrodes.

2 RESULTS AND DISCUSSION

2.1 Super-stable Polyanilines

Polyaniline is a p-type polymer that has been explored for years as a battery cathode in lithium metal batteries. Polyaniline reversibly can achieve doping levels of about 0.5 (3.5 V *vs.* Li/Li^+), but a doping level of 1.0 is possible in principle (beyond 3.5 V *vs.* Li/Li^+). We have demonstrated two separate approaches to significantly enhance the doping level to near unity. In the first approach, we synthesize polyaniline in the presnce of a strong polyacid, which acts as a dopant. This yielded a reversible stability up to 4.5 V *vs.* Li/Li^+ and a doping level of 0.8, Figure 1.[3] In a second approach we blended polyaniline with a weak polyacid, in which the polyacid was partially ionized. This lended a reversible capacity up to 4.2 V *vs.* Li/Li^+ due to the buffering effect of the polyacid.[4]

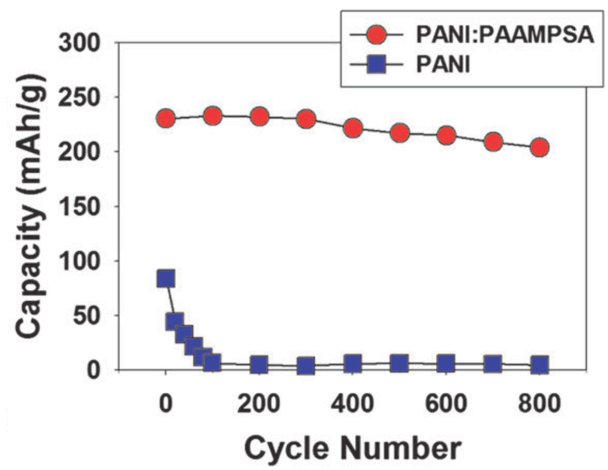

Figure 1: Discharge capacity of polyaniline (PANI) and polyaniline:poly(2-acrylamido-2-methylpropane sulfonic acid) (PANI:PAAMPSA) cycled between 2.5 and 4.5 V *vs.* Li/Li^+. Figure adapted from Jeon, J.-W.; Ma, Y.; Mike, J. F.; Shao, L.; Balbuena, P. B.; Lutkenhaus, J. L. Oxidatively stable polyaniline:polyacid electrodes for electrochemical energy storage. *Physical Chemistry Chemical Physics* **2013,** *15* (24), 9654-9662.

2.2 Spray-on Battery Electrodes

Perhaps one of the most interesting aspects of electroactive polymers is their adaptability to unconventional battery processing methods, such as spraying. Spray-on batteries are of potential interest for the area of structural energy storage, where a battery is seamlessly integrated into structural panels or other surfaces. We use spray-assisted layer-by-layer assembly to assemble hybrid electrodes containing polyaniline nanofibers and graphene oxide sheets in a water-based approach, Figure 2.[5] The electrodes are then reduced, resulting electrode is highly porous and conductive.

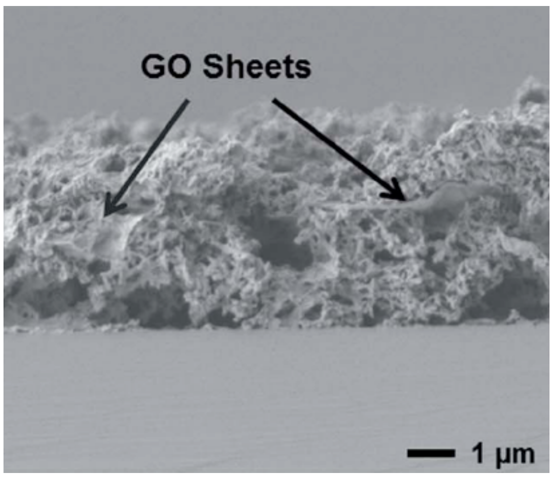

Figure 2: Cross-sectional scanning electron microscope images of polyaniline nanofiber/graphene oxide spray-assisted layer-by-layer electrodes. Adapted from Kwon, S. R.; Jeon, J.-W.; Lutkenhaus, J. L. Sprayable, paintable layer-by-layer polyaniline nanofiber/graphene electrodes. *RSC Advances* **2015,** *5* (20), 14994-15001.

2.3 Flexible and Tough Hybrid Electrodes

Another advantage of electroactive polymers is that they have the potential to impart unusual flexibility and toughness into otherwise brittle metal oxides in a hybrid electrode configuration. We have blended V_2O_5, a commonly explored Li-ion battery cathode, with an electroactive polymer binder. The block copolymer contains ion-conducting poly(ethylene oxide) blocks and electron-conducting poly(3-hexylthiophene) blocks. Only 5 wt % polymer is required to triple the flexibility of V_2O_5, and electrodes comprised of 10 wt % polymer have unusually high toughness (293 kJ/m^3) and specific energy (530 Wh/kg), both higher than reduced graphene oxide paper electrodes. This yields an unusual combination of energy and toughness not commonly found in metal oxides, Figure 3.[6]

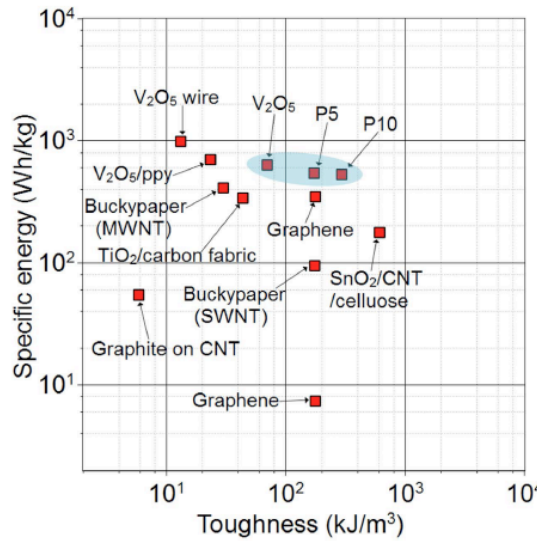

Figure 3: An Ashby plot of specific energy vs. toughness. Specific energy is reported as per mass of electrode. Adapted from An H, Mike J, Smith KA, Swank L, Lin Y-H, L. Pesek S, et al. Highly Flexible Self-Assembled V2O5 Cathodes Enabled by Conducting Diblock Copolymers. Scientific Reports. 2015;5:14166.

3 CONCLUSION

The outlook for electroactive polymers is very promising with new advances in chemistry, processing, and composites. These may one day lead to ultra flexible or structural energy storage systems enabled by "plastic power". Challenges still remain with addressing stability in the electroactive polymer, processing, and its interactions with other electrode materials. Our future directions lie in organic radical polymers and in structural electrodes.

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