

Effect of Counter-Ion Charge and Hydration on Poly(3,4-ethylenedioxythiophene) (PEDOT) Studied with X-ray Photoelectron Spectroscopy

S.A. Spanninga¹, Z. Chen^{1,2}, and D.C. Martin^{1,3,4}

1 Macromolecular Science and Engineering Center, University of Michigan, Ann Arbor, MI 48109

2 Department of Chemistry, University of Michigan, Ann Arbor, MI 48109

3 Materials Science and Engineering, University of Delaware, Newark, Delaware, 19716

4 Department of Materials Science and Engineering, Ann Arbor, MI 48109

Poly(3,4-ethylenedioxythiophene) (PEDOT), is a highly conductive (~300 S/cm) [1], π conjugated polymer that can be synthesized by either oxidative chemical, organic vapor, or by electrochemical polymerization. PEDOT applications include anti-static coatings and organic light emitting devices [1], but more recent studies have taken advantage of both the electronic and ionic conductivity for the use of PEDOT as a biological tissue interfacing agent [2, 3].

While previous work focused on how different counter-ions affected both on the polymer surface morphology and electrical properties of the PEDOT polymer film [4,5], the motivation driving this research was to deduce whether anion hydration was indeed the driving force dictating PEDOT counter-ion incorporation. X-ray photoelectron spectroscopy (XPS) was used to deduce the respective PEDOT film's chemical composition.

In order to deduce whether the anionic hydration trend, based upon the Hofmeister Series [6-8], coincides with PEDOT counter-ion affinity, a systematic study of 3,4-ethylenedioxythiophene with various differently hydrated anion mixtures (most to least hydrated anions) were mixed and an electrochemically polymerized PEDOT film was deposited. The anions used were: (1) $\text{C}_6\text{H}_5\text{O}_7^{-3}$, (2) CO_3^{-2} , (3) $\text{S}_2\text{O}_3^{-2}$, (4) $\text{C}_2\text{H}_3\text{O}_2^-$, (5) HPO_4^{-2} , (6) H_2PO_4^- , (7) Cl^- , and (8) Br^- followed by either NO_3^- or ClO_4^- additions. The C 1s and S 2p characteristic region results are shown in Figure 1 and 2 respectively.

The C 1s region, before the addition of $\text{Na}_2\text{S}_2\text{O}_3$ to the mixture, was dominated by COO^- (~289 eV). Once the addition of $\text{Na}_2\text{S}_2\text{O}_3$ was made, the $\text{PEDOT}^+\text{S}_2\text{O}_3^{-2}$ low, broad S 2p spin-split doublet appeared and displayed dominance over all the other anions regardless of their anionic hydration state. Lack of $\text{PEDOT}^+\text{CO}_3^{-2}$ (~289 eV) and $\text{PEDOT}^+\text{COO}^-$ (~289 eV) signals in C 1s, phosphate signal in the P 2p (not shown), ClO_4^- and Cl^- signals in the Cl 2p (not shown) [10], Br^- signal in the Br 3d (not shown), and NO_3^- in the N 1s (not shown), eliminates the possibility of the other anions, CaCO_3 , $\text{NaC}_2\text{H}_3\text{O}_2$, Na_2HPO_4 , NaH_2PO_4 , NaCl , LiBr , NaNO_3 , and LiClO_4 , as acting as PEDOT counter-ions.

References

- [1] L. Groenendaal et. al., *Adv. Mater.* 12 (2000) 481.
- [2] D.H. Kim et al., *Adv. Funct. Mater.* 17 (2007) 79.
- [3] S.M. Richardson-Burns et al., *Biomaterials* 28 (2007) 1539.
- [4] S.A. Spanninga et al., *J. Phys. Chem. C* 113 (2009) 5585.
- [5] J. Yang et al., *J. Biomater. Sci. Polymer Edn.*, 18 (2007) 1075.

- [6] W. Kunz et al., *Curr. Opin. Colloid Interface Sci.* 9 (2004) 19.
 [7] Y. Marcus, *J. Soln. Chem.* 23 (1994) 831.
 [8] H.D.B. Jenkins et al., *Chem. Rev.* 95 (1995) 2695.

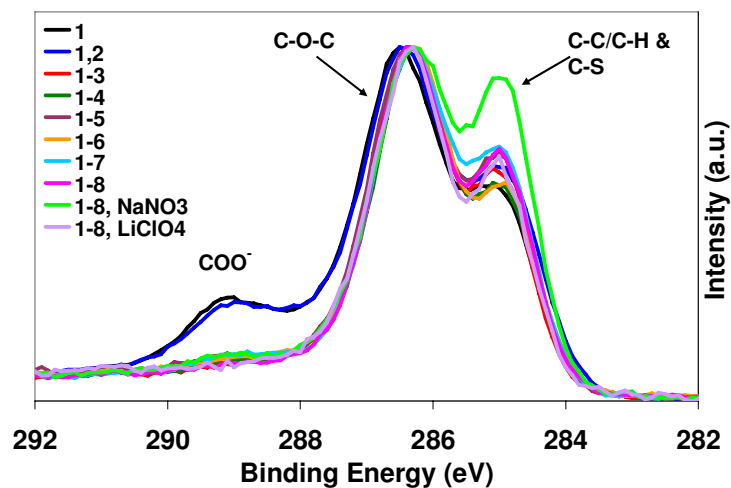


FIG. 1. Characteristic C 1s Region

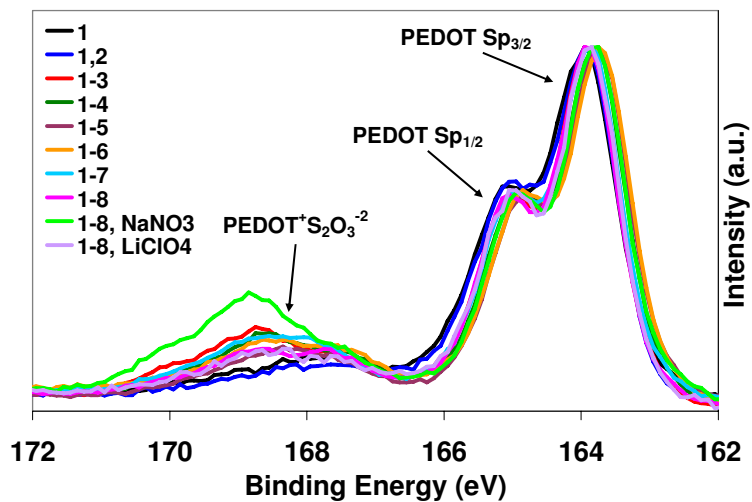


FIG. 2. Characteristic S 2p Region