

PEDOT:PSS-DVS Crosslinking Reaction Monitored via ATR-FTIR for Air Cathode Application in Microbial Fuel Cells

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Abstract —

Microbial fuel cells (MFCs) intended for at-risk communities lacking sources of clean water and electricity could be more economically produced by the implementation of biomolecular air cathode technology: an encapsulated enzyme within an electrically conductive nonwoven spunbound polymer such as PEDOT:PSS. While PEDOT:PSS may be spunbound and boasts high conductivity, it is prone to delamination and redispersion due to its water solubility. We report the analysis of crosslinking reactions with divinyl sulfone (DVS) in order to improve the durability and insolubility of conductive PEDOT:PSS fibers. Analytical characterization of crosslinking PEDOT:PSS with DVS using time-lapsed ATR-FTIR spectroscopy in concentrated solutions permits a clear characterization of PEDOT:PSS-DVS crosslinking kinetics and structure.

I. INTRODUCTION

In 2015, the Joint Monitoring Programme sponsored by the World Health Organization/UNICEF announced that one in ten persons is without access to clean water accounting for 663 million people (319 million of which were located in Sub-Saharan Africa) of an estimated 7.3 billion at the time of study [1]. Furthermore, UNICEF has reported that 6,000 children die daily of water-related diseases accounting for an overwhelming fraction of 2.2 million diarrhea-caused fatalities annually [2]. In conjunction with a lack of safe drinking water, impoverished areas also tend to lack access to electricity. The International Energy Agency asserted that in 2014, 634 million persons in Africa lacked access to electricity, of which 632 million resided in Sub-Saharan Africa. In total, 1.2 billion persons globally lacked electricity as of 2014 [3], a basic amenity that powers essential daily processes such as cooking.

The lack of clean drinking water presents a global public health crisis with a distinct call to action: first to limit water expenditure, and second to advance water remediation technology to provide an inexpensive, user-friendly, self-powered, and reliable method of providing clean water. One method of wastewater treatment, bioremediation, is the use of bacteria to digest otherwise harmful compounds in their

immediate environment, in turn generating non-toxic waste waters [4]. The microbial fuel cell (MFC) can potentially make use of bioremediation to clean contaminated water while generating electricity, thus, presenting a self-powered water purification system [5].

An MFC operates similarly to a battery. Microbial digestion of waste water in an anode compartment produces carbon dioxide, protons and electrons. The electrons then travel by direct contact through bacterial pili - a hair-like structure located on the surface of many bacteria which function as the fuel cell anode. From the anode, the electrons travel to an electron load onto the cathode. The cathode captures these electrons and protons from the anode as it reduces oxygen from the air to form water [6]. A general diagram of a typical amicrobial fuel cell is provided in Fig. 1.

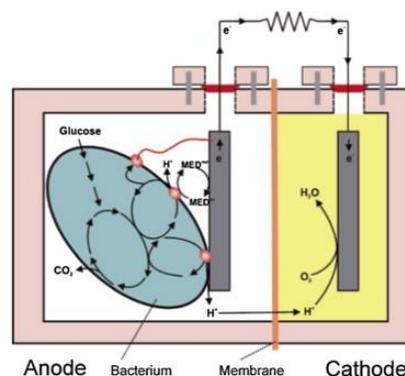


Fig. 1. An MFC comprises of anode and cathode compartments [7]

Many current cathode technologies utilize cost prohibitive precious metals as cathode catalysts [8-10]. Such technologies would be beyond the economic reach of families in underdeveloped communities, such as Sub-Saharan Africa [11]. Hence, we have interest in investigating the viability of renewable laccase enzyme cathode catalysts due to recent cost-diminishing manufacturing scale economy. Laccase catalyzes the reduction of a dioxygen molecule using four electrons and four protons to create two water molecules [12-15].



The current state of the art MFC technology demonstrates laccase catalysis in air cathodes, yet the technology is neither efficient nor economically viable [12-14]. An ideal air cathode features a redox active enzyme, e.g. laccase, encapsulated in an electrically conductive polymer processed into a nonwoven fiber to permit efficient reduction of atmospheric oxygen. However, such a system has not yet been demonstrated. A reliably potential polymer is Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS). Since PEDOT:PSS films are susceptible to delamination and dispersion, interest for various applications exists in crosslinking the polymer that not only results in an insoluble film, but further a film with greater conductivity than the non-crosslinked control [16-18].

Dr. Mantione and coworkers, of the University of Basque Country, claim room temperature crosslinking of PEDOT:PSS films using divinyl sulfone (DVS) [16]. Reacted films provide visibly greater resilience to re-dispersion than unreacted films, but do not identify the reaction mechanism. Changes in ^1H NMR spectra are consistent with more than one reaction chemistries, possibly involving PSS and/or diethylene glycol. The latter would not result in chemical crosslinks with PEDOT:PSS. Additional characterizations using UV-Vis-NIR spectroscopy, Raman spectroscopy, and FTIR spectroscopy show little difference from non-crosslinked controls [16].

This work re-examines the reaction between PEDOT:PSS and DVS using time-resolved, 2-D correlation ATR-FTIR spectroscopy. Using both experimental evidence and quantum chemical calculations, we find that PSS and DVS can participate in a crosslinking reaction.

II. MATERIALS AND METHODS

A. Materials

Poly(3,4-ethylene dioxythiophene)-poly(styrene sulfonate) (PEDOT: PSS) and divinyl sulfone (DVS), see Fig. 2, were purchased from Sigma Aldrich. The 1.3 wt.% PEDOT:PSS dispersion in water contains 0.5 wt. % PEDOT content and 0.8 wt. % PSS content. DVS is specified at 97% purity containing less than 650 ppm hydroquinone as an inhibitor. Reactions between PEDOT:PSS and DVS are initiated by adding 2.0% v/v DVS and 1.3 wt.% PEDOT:PSS.

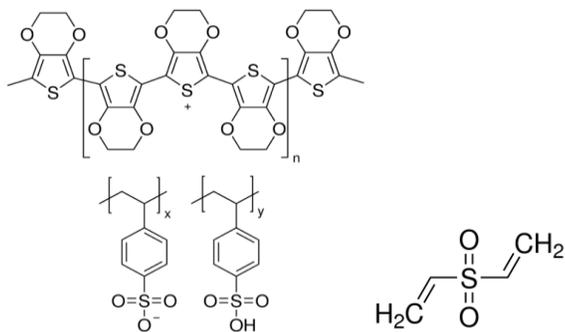


Fig. 2. Chemical structures of PEDOT:PSS (left) and DVS (right).

B. Attenuated Total Reflection-Fourier Transform Infrared Resonance Spectroscopy (ATR-FTIR)

ATR-FTIR spectrum measurements were collected using a Bruker Vertex 70 FT-IR spectrometer equipped with a MIRacle ATR stage. Spectra were analyzed using OPUS 6.5 software. 2D correlation analysis was performed using a custom JAVA application written by and available from Prof. Lustig.

Separate ATR-FTIR spectra of 2.0 wt.% DVS and 1.3 wt. % PEDOT:PSS aqueous compositions were collected relative to pure water reference spectra from 550 cm^{-1} to 4000 cm^{-1} . For time-lapsed PEDOT:PSS-DVS reaction studies, a reference spectra was collected while the ATR crystal was covered with water. These aqueous dispersions were sealed over the ATR crystal to prevent water evaporation. Each spectrum was collected by averaging 24 interferograms over ca. 20 seconds. Spectra were collected every ten minutes over 16.5 hours.

C. Quantum Thermochemical Calculations

All calculations were performed using the density functional theory electronic structure program DMol3 [19, 20] with graphical displays generated with Materials Studio [21]. The Perdew-Burke-Ernzerhof (PBE) non-local correlation [22] was used for the exchange and correlation potentials with restricted spin polarization and fine DNP (loosely defined as double-numeric + polarization) numerical basis sets [19] with 4A cut-off. Atomic cores are described with the all-electron treatment. self-consistent field iterations were considered converged with 10^{-6} Ha tolerance and no thermal smearing was used in the orbital occupancy. Molecular geometries were refined via energy optimizations in which convergence tolerance criteria included energy changes less than 10^{-5} Ha, maximum forces less than 0.002 Ha/\AA and maximum displacements less than 0.005 \AA . Thermodynamic properties such as entropy, enthalpy, and Gibbs energy are computed at finite temperatures after fine geometric optimization and vibrational analysis or Hessian evaluation. Vibrational, rotational, and translational contributions to the molecular partition function are computed according to the standard statistical mechanics in the ideal gas approximation [23]. The geometry of molecular structures is optimized by minimizing the total energy.

III. RESULTS AND DISCUSSION

Evidence for reaction between PEDOT:PSS and DVS is shown through a series of time-lapsed ATR-FTIR spectra. Variances in the spectra caused by both disappearance of DVS and changes to polystyrene sulfonate can be easily elucidated using the 2D correlation method [24, 25]. Both the synchronous, Φ , and asynchronous, Ψ , correlation intensities of the dynamic spectra are shown in Fig. 3. The synchronous correlation intensity indicates the degree of coherence between two signals (wavelengths and their associated intensities) that are measured simultaneously. Peak positions at 1249, 1301, and 1388 cm^{-1} associated with aqueous DVS are synchronously correlated (share positive Φ) as they decrease concomitantly through the time series. Meanwhile the appearance of a peak at 1263 cm^{-1} is oppositely correlated with the disappearance of DVS (shares negative Φ cross correlations). The asynchronous correlation intensity between two peaks represents independent or mutually

out of phase time dependent intensity of the dipole-transition moments. Since cross peaks do occur, the 1263 cm^{-1} and DVS absorptions are decoupled.

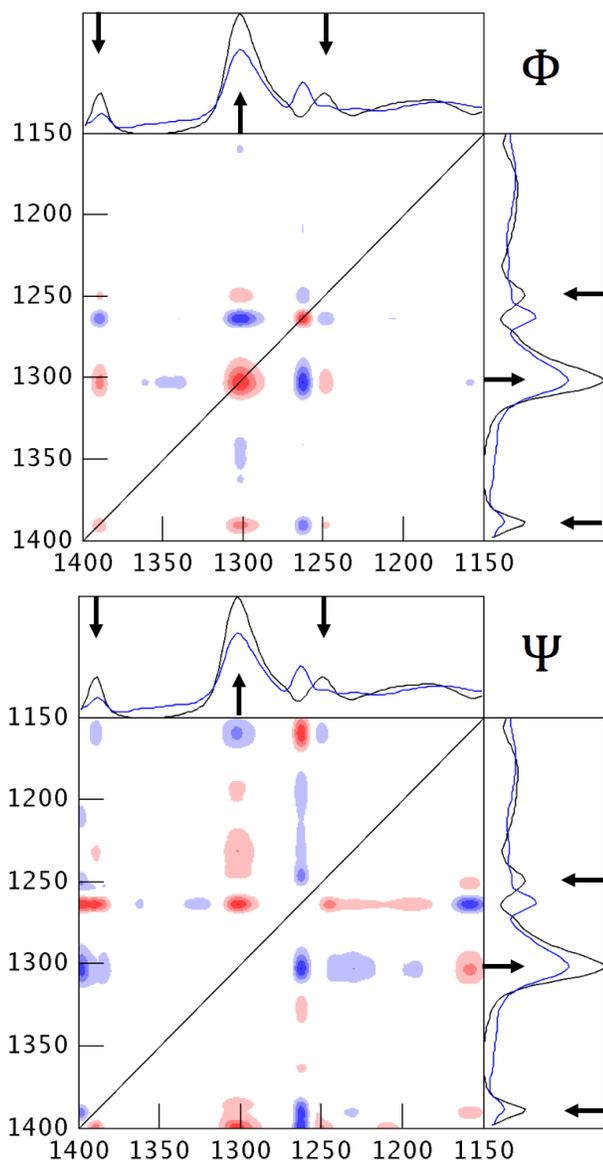


Fig. 3. Synchronous (top) and asynchronous (bottom) intensities as functions of wavenumber, cm^{-1} , (abscissa and ordinate). Positive intensity is denoted by red color and negative intensity is denoted by blue color. Peak positions common to aqueous DVS control spectra are marked by black arrows. Axis spectra contain the first spectrum (black) and the last spectrum (blue) in the time series.

Since the cross peaks in Φ and Ψ for the 1263 cm^{-1} and the DVS absorptions are opposite in sign, the dipole intensity increase at 1263 cm^{-1} occurs faster than the DVS dipole intensity decrease. The shape symmetry of the Φ and Ψ peaks indicates these are independent dipole transition moments, not due to environment-based wavenumber shifting or broadening validating the claim that reaction of interest is, in fact, occurring.

The appearance of the new 1263 cm^{-1} absorbance indicates it is signature of the observed reaction product. We expect the reaction to form a vinyl sulfone ethyl sulfate structure, shown

in Fig. 4 as the DVS vinyl group is reactive with the PSS sulfonic acid. Quantum chemical calculations of this structure's vibrational states and molecular partition function [19-23] provide consistent evidence for this hypothesis.

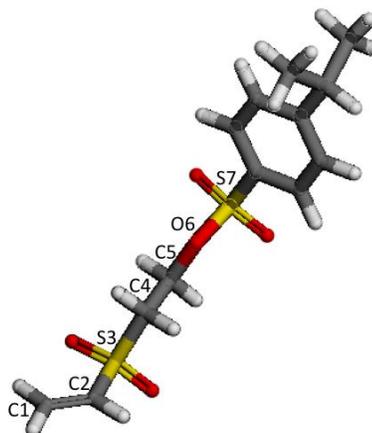


Fig. 4. Vinyl sulfone ethyl sulfonate fragment indicating the expected product from the reaction between DVS and PSS.

The structure is predicted to have significant vibrational absorptions at 1205 cm^{-1} (CH_2 wagging at C4), 1267 cm^{-1} (CH_2 twisting at C5), 1304 cm^{-1} (in phase CH_2 twisting at C4 and C5), 1320 cm^{-1} (in phase CH_2 twisting at C5 and OSO scissoring at S7), and 1384 cm^{-1} (CH_2 scissoring at C1). Each of these absorbances are detected in Fig. 3. Most significantly, the match between 1263 cm^{-1} (observed) and 1267 cm^{-1} (predicted) is within accepted accuracy for the theoretical method. Statistical thermodynamic predictions are consistent with this reaction product. At room temperature the ideal phase reaction Gibbs energy is -108 kcal/mol from which the reaction entropy is -112 cal/mol-K and the reaction enthalpy is -142 kcal/mol. Thus the reaction is energetically favored at room temperature despite a small loss in entropy due to combining two molecules.

IV. CONCLUSION

The study undertaken provides valuable insight into the reaction between PEDOT:PSS and DVS that can result in physical crosslinking. Changes in the infrared spectra occur exclusively in regions that correspond to either alkene or sulfonic groups. Since PEDOT:PSS has no reactive alkene groups, and DVS has no sulfonic acid groups, it is reasonable to conclude that the changes in the spectra are a result of an interaction between the two molecules. The proposed product structure enables a crosslinked network between PSS macromolecules. The data collected provides material for future study in crosslinking kinetics as well as opportunity to generate a more durable, and insoluble, PEDOT:PSS fiber for incorporation into air cathodes as per the purpose of the literature.

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