

Tuning Selectivity of Electrochemical Sensors through Polymer Modifications

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Summary:

Electrochemical sensors are highly promising for emerging applications, including health and environmental monitoring. Yet, a key bottleneck of today's sensors is limited selectivity. While electrode material development can enhance sensor performance, it is often insufficient to achieve the desired selectivity. Here, we introduce a different approach: modifying electrode surfaces with neutral polymeric coatings. Specifically, we demonstrate that poly(4-vinylpyridine) (P4VP) coatings deposited on glassy carbon electrodes systematically shift the oxidation potentials of ascorbic acid (AA) and serotonin (5-HT), thereby separating their oxidation peaks and enabling simultaneous detection in mixture. Importantly, we show that this concept is not limited to this specific example, but can be expanded to varying polymers, additional biomarkers (i.e., estradiol and melatonin), and other carbon electrode materials. Overall, this work demonstrates an alternative strategy to controlling the apparent oxidation potential and selectivity of electrochemical sensors, promising for next-generation sensing applications.

Keywords: electrochemical sensor, selectivity, polymer coating, multi-analyte detection, biomarker

Background, Motivation and Objective

Electrochemical sensors are promising for health applications due to their high sensitivity, repeatability, and compatibility with miniaturized, low-cost platforms [1]. However, their translation into real applications is hindered by limited selectivity: many small-molecule biomarkers, such as 5-HT and AA, exhibit similar oxidation potentials and produce overlapping voltammetric signals that prevent molecular discrimination. Existing approaches to improve selectivity often rely on specific binding receptors [2], but frequently face issues with stability and regeneration due to the strong binding affinity between receptor and target analyte. Receptor-free sensors bear the advantage of repeatability, and material design can improve selectivity; however, this is rarely sufficient to overcome selectivity limitations in complex, real-world fluids.

An alternative strategy is the use of polymeric coatings that modify the electrochemical interface. The most commonly employed polymers are conductive (e.g., PEDOT) or charged (e.g., Nafion [3]), while neutral polymers have received little attention, as they are generally considered to impede diffusion. We show that neutral polymeric coatings are an effective strategy for altering sensor selectivity, providing a novel and so far unexplored route towards selectivity.

Description of the New Method or System

The rationale of our work is to modulate oxidation potentials and currents through polymeric coatings [4]. To this end, we deposit commercial polymers onto glassy carbon electrodes (GCE) via drop-casting. P4VP was selected as the primary coating material because its pyridinic nitrogen can interact with a wide range of molecules, acting as a strong Lewis base and efficient hydrogen-bond acceptor. We hypothesize that polymer-biomarker interactions alter the electron distribution of the biomarker and its adsorption at the electrode interface, resulting in shifts in oxidation potential. We strengthen this hypothesis through chronocoulometry and Fourier-transform infrared spectroscopy (FTIR).

We evaluate the effect of polymeric coatings on the electrochemical detection of ascorbic acid (AA), serotonin (5-HT), melatonin (Mel), and estradiol (E2), chosen for their relevance in clinical applications. We demonstrate that polymeric coatings can selectively modify the oxidation potentials of these biomarkers, thereby enhancing system selectivity, and that this concept extends to other carbon electrode materials and multiple commercial polymers.

Results

The effect of P4VP coatings on GCE is shown in **Fig. 1**. On a bare GCE, the oxidation potentials of AA and 5-HT overlap in the potential range of 0.2 to 0.4 V (**Fig. 1a**). This overlap becomes particularly problematic when measuring the two analytes in a mixture, where physiological AA concentrations exceed 5-HT by orders of magnitude. In fact, in the mixture, the 5-HT signal is obscured by the broad AA shoulder (**Fig. 1b**). In contrast, applying a P4VP coating shifts the 5-HT peak to higher potentials and the AA peak to lower potentials (**Fig. 1c**), yielding a clear peak separation that persists in mixture and enables analyte discrimination (**Fig. 1d**).

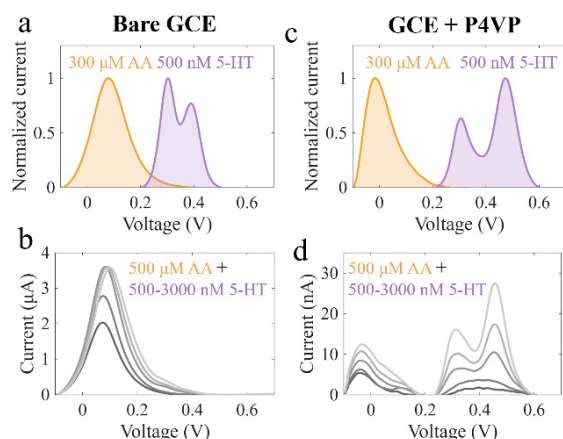


Fig. 1. (a) normalized SWV of ascorbic acid (AA) and serotonin (5-HT) measured as single analytes on a bare GCE. (b) Corresponding mixture measurement (c) normalized SWD detection of AA and 5-HT as single analytes on P4VP-coated GCE. (d) Corresponding mixture measurement [4].

Chronocoulometry and FTIR reveal that the P4VP coating enhances AA adsorption on the GCE surface while reducing 5-HT adsorption, consistent with the observed oxidation potential shifts. FTIR further confirms significant hydrogen bonding between both analytes and P4VP.

Importantly, this concept is not limited to P4VP and these two analytes, but extends to other polymer coatings and biomarkers, each displaying polymer-specific oxidation potentials (**Fig. 2**), as well as to other carbon electrode materials [5]. The ability to control oxidation potentials through a simple polymeric coating represents a significant step towards tunable sensor selectivity: sensor arrays featuring distinct polymeric layers could enable diverse and orthogonal analyte detection, and we have recently shown that polymer-modified electrodes combined with machine learning can differentiate multiple analytes in complex mixtures [6].

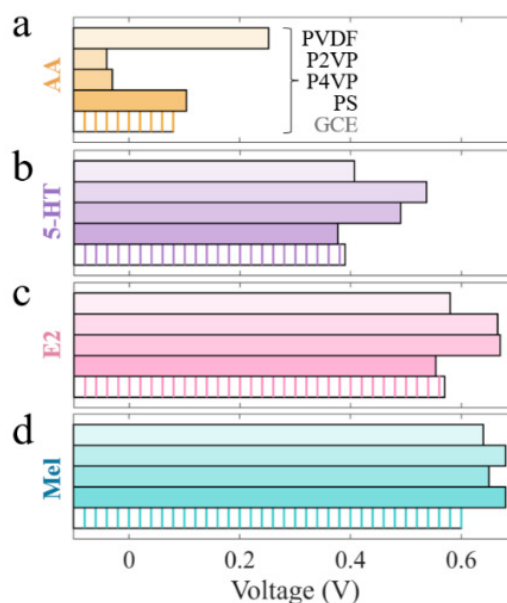


Fig. 2. Oxidation potential of AA, 5-HT, E2, and Mel on the bare GCE and various polymeric coatings (bottom to top: PS, P4VP, P2VP, PVDF) [4].

Conclusion

Polymer coatings offer a simple route to tune the oxidation potentials of electrochemical sensors. We demonstrate that P4VP coatings effectively separate the oxidation potentials of AA and 5-HT, enabling their detection in mixture. This concept extends to various polymers and additional biomarkers, offering a unique handle over the selectivity of label-free electrochemical sensors.

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