Article

Rapid and Direct Perfluorooctanoic Acid Sensing with Selective Ionomer Coatings on Screen-Printed Electrodes under Environmentally Relevant Concentrations

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ABSTRACT: Per- and polyfluoroalkyl substances (PFASs) pose a significant health threat to humans at trace levels. Because of its ubiquity across the globe, there have been intense efforts to rapidly quantify PFASs in the environment while also mitigating their release. This work reports an electrochemical sensor with a selective perfluorinated anion exchange ionomer (PFAEI) coating for direct sensing of perfluorooctanoic acid (PFOA)—a type of PFAS. Notably, the sensor operates without the need of redox probes and has a limit of detection around 6.51 ± 0.2 ppb (15 nM) in buffered deionized water and drinking water. By testing the sensor with different ionomer electrode coatings, it was inferred that the PFAEI favors PFOA anions over other competing anions in solution through a combination of electrostatic and van der Waal interactions.
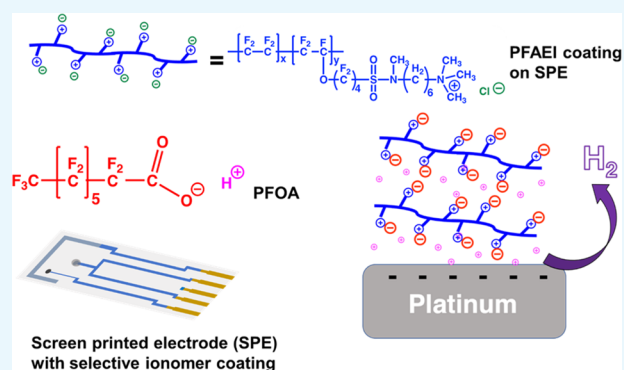
INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are a byproduct of the amazing materials that make up our everyday life (e.g., fire-fighting foams, lubricants, non-stick cookware, coatings for textiles, carpet, paper, food packaging, etc.).[1−7] These chemicals, and their high-molecular-weight polymer analogues (e.g., polytetrafluoroethylene), are termed "Forever Chemicals" because of their exceptional chemical stability in the presence of oxidizers and extreme pH values. The miracles wrought by perfluorinated polymers have unfortunately led to the release of PFASs into the environment. As such, PFASs pose serious remediation challenges and threats to public health.[8,9] For example, bioaccumulation of PFASs in humans is well-documented and cause cancer,[10] estrogen disruption,[11] protein misfolding,[12] birth defects, and other health risks.[13−17] These challenges have spurred research in technologies for PFAS sensing,[18] removal,[19−21] and destruction upon sequestration.[22−24]

Traditional detection methods for PFASs in environmental matrices rely upon on complex machinery such as LC−MS and HPLC. These instruments are bulky and expensive and require time-consuming sample preparation. Although accurate and reliable, they cannot quantify PFAS contaminants within a minute or less. Because field workers may wish to identify PFAS concentrations rapidly or to sense a containment vessel leak, there is a critical need to develop economical and straightforward PFAS sensing technologies with broad applicability.

Electrochemical detection platforms[25−29] are an enticing prospect for PFAS sensing in the field as it is portable, robust, and economical. Electrochemical sensors have been shown to detect PFASs in a diverse class of matrices ranging from environmental water to blood serum, with concentration of perfluorooctanoic acid (PFOA) ranging from 15.7 to 128 ppb, especially in a community residing close to PFAS production facilities.[30] A notable electrochemical sensor by Karimian et al.[31] showed a level of detection (LOD) of 0.04 nM (17ppt) for PFOS in deionized (DI) water using a template-assisted molecularly imprinted polymer. This sensor provides indirect detection of PFOS because it relies upon the ferrocenecarboxylic acid redox-active probe. The electrochemical signal from this probe is quenched by the presence of PFOS. The strong affinity of PFOS for common electrodes, like gold, necessitates a molecularly imprinted polymer to stymie PFOS adsorption. Without a porous polymer coating, any amount of PFOS would quickly saturate the electrode response. There are also other ferrocene-based redox probes for electrochemical sensing of PFOS,[32,33] some with molecularly imprinted polymers. In one of these other demonstrations,[32] GenX, which is also a similar class of perfluoroalkyl acids, was quantified in actual
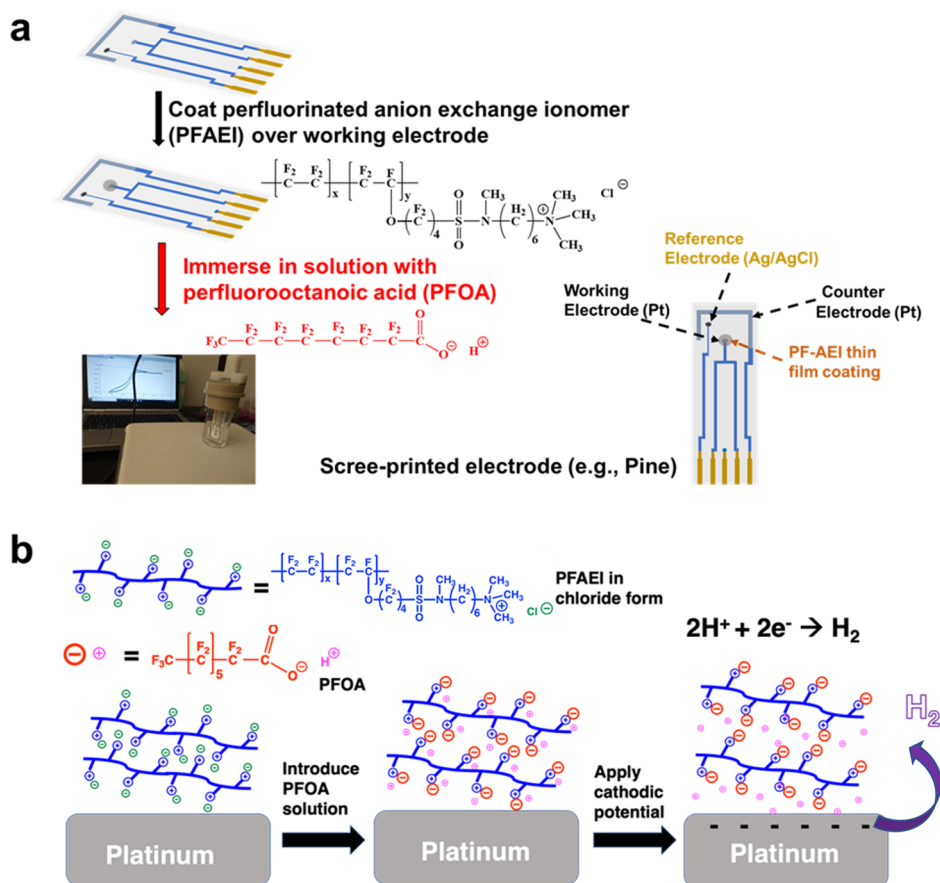
Figure 1. (a) Preparation of PFAEI coating on commercial SPE configurations. (b) Proposed mechanism for PFOA sensing with PFAEI coating on the SPE.

river water at concentrations approaching ∼1 pM. A drawback of these indirect electrochemical sensors for PFASs is that they require the addition of redox-active probes. The need to carry chemical reagents with the sensor is inconvenient for portable electronics, like smartphones, and can complicate the sensor design.

In this letter, a rapid and direct electrochemical sensor for PFOA is demonstrated through the appropriate selection of a selective ionomer coating [i.e., a perfluorinated anion exchange ionomer (PFAEI)] and adoption of commercially available screen-printed electrodes (SPEs). The ability to perform direct sensing of PFOA was attributed to electrostatic, van der Waal, and hydrophobic interactions[34,35] between the PFAEI coating and PFOA. These interactions were inferred by testing other ionomer coatings that consisted of a hydrocarbon anion exchange ionomer [quaternary benzyl pyridinium chloride poly(arylene ether sulfone) (QPPSf)], a hydrocarbon cation exchange ionomer [sulfonic acid polyether ether ketone (SPEEK)], and a perfluorinated cation exchange ionomer (Nafion—a type of perfluorosulfonic acid). Figure S1 provides the chemical structures of the various ionomer coatings assessed in this work. The other ionomer coatings minus the PFAEI were ineffective for sensing and highlighted the need for anion exchange ionomers with perfluoro backbones and side chains to promote the van der Waal interactions and quaternary ammonium groups for PFOA anion exchange.

■ RESULTS AND DISCUSSION

Figure 1a illustrates a SPE with a PFAEI coating for PFOA sensing. SPEs are often used for sensing in biological applications. Because of the sensors' planar nature, they are conducive for the deposition of PFAEI and other ionomer coatings on the electrodes. A similar class of perfluorinated polycationic ionomers, specifically Tosflex IE-SA 48-based anion exchange ionomer-modified glassy carbon electrodes, was previously demonstrated in the trace level detection and speciation of heavy metal ions (Hg^{2+} and Cu^{2+}) and toxic pollutants like 2-napthol in waters.[36–39] One advantage of the PFAEI coating studied here is that it prevents direct PFOA adsorption on platinum. With respect to the sensing mechanism, it was postulated that the tethered quaternary ammonium moiety in the PFAEI exchanges with the PFOA anion in solution. The perfluoro-nature of the PFAEI backbone is conducive for PFOA anion adsorption and ion pairing with the tethered quaternary ammonium. Hence, both van der Waal and electrostatic interactions work cooperatively for promoting PFOA uptake in the PFAEI. The perfluoro backbone favored the perfluoro chain in PFOA, and the quaternary ammonium groups favorably interacted with the carboxylate anion in PFOA. The proton released from the exchanged PFOA can permeate the PFAEI as the quaternary ammonium groups are screened by the PFOA anion (i.e., poorly dissociated), and protons break and form bonds with water. Hence, the protons can easily permeate through anion exchange materials despite other cations resisting permeation due to the Donnan exclusion (note: this is a well-known phenomenon as it is
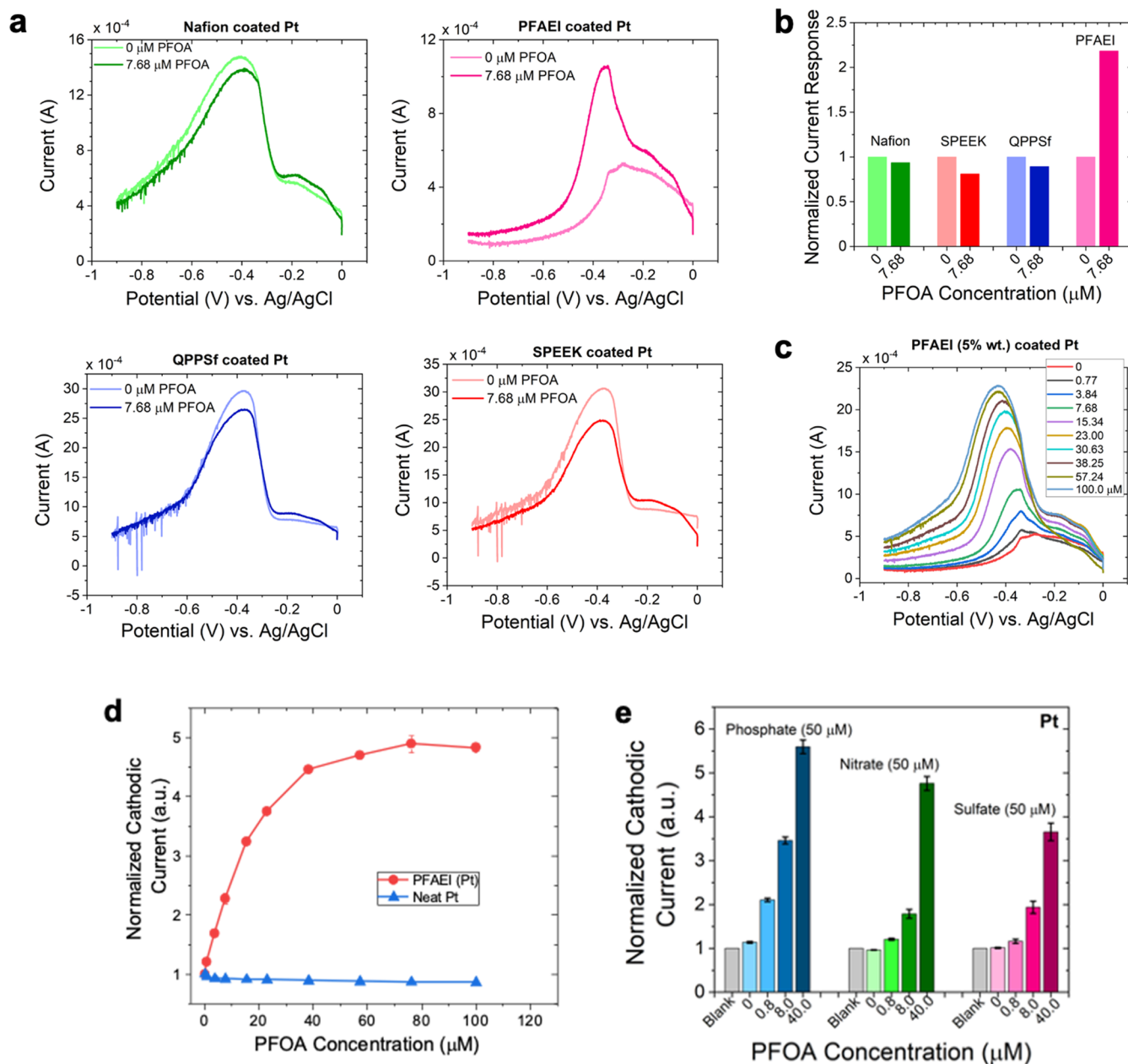
Figure 2. (a) SWV of platinum wire working electrode data with different ionomers at a PFOA concentration of 7.68 μM; (b) normalized current response with different ionomers at −0.40 V vs Ag/AgCl; (c) SWV of wire data with PFAEI coating with various PFOA concentrations at −0.40 V vs Ag/AgCl. (d) Normalized current responses as a function of PFOA for a given cathodic peak potential for the PFAEI ionomer-coated Pt and neat Pt electrode @ −0.40 V vs Ag/AgCl; and (e) bar graphs with different interfering anions for the platinum-coated PFAEI measured at an applied potential of −0.47 V vs Ag/AgCl using chronoamperometry.

difficult to devise anion exchange membranes that resist acid crossover).[40] The protons then migrate to the negatively biased electrode across the PFAEI−PFOA anion material to undergo the hydrogen evolution reaction (HER). The current response from HER was used to detect and quantify PFOA in solution. Figure 1b conveys the PFOA anion exchange with the PFAEI, proton permeation in the PFAEI to the cathode, and the HER process.

Figure 2a compares the current response from square wave voltammetry (SWV) experiments of a platinum wire working electrode with various ionomer coatings immersed in 7.68 μM PFOA buffered solution. Figure 2b compares the normalized current at −0.4 V versus Ag/AgCl for the platinum working electrodes with different ionomer coatings. These two plots

unequivocally demonstrate that the PFAEI material is the best coating for sensing PFOA. The cation exchange ionomers, Nafion and SPEEK, cannot adsorb PFOA anions due to Donnan exclusion. The QPPSf anion exchange ionomer has a hydrocarbon backbone that is not conducive for PFOA adsorption. As discussed earlier, it is the perfluoro backbone and quaternary ammonium groups of the PFAEI that favor PFOA anion adsorption.

After identifying the most effective ionomer coating, SWV was performed with the platinum working electrode coated with the PFAEI with solutions that contained different PFOA concentrations (Figure 2c). The range was 0.77−100 μM. As the PFOA concentration increased, the current response
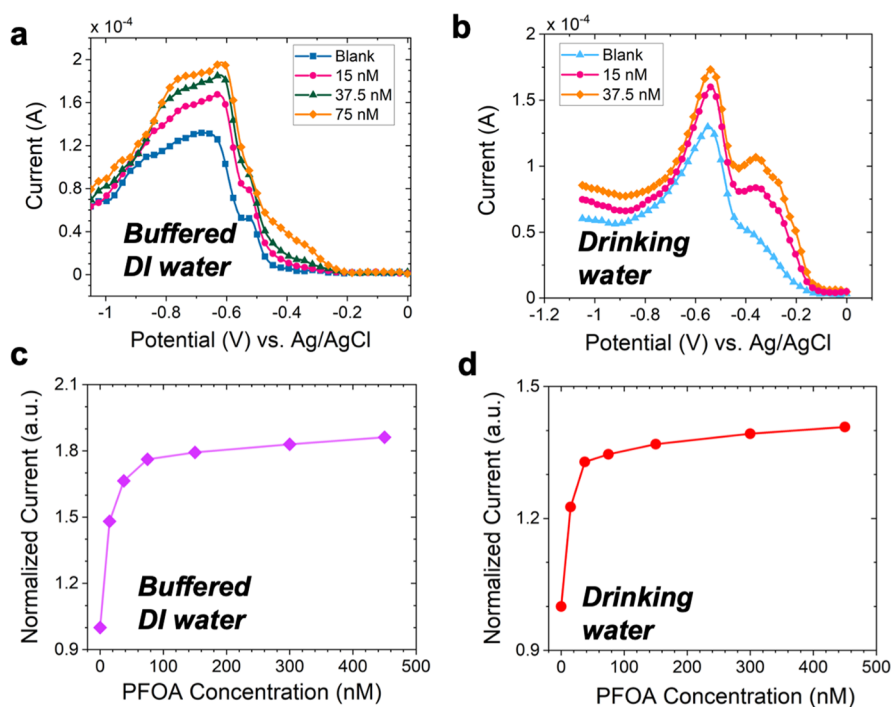
Figure 3. SWV data of SPE with PFAEI coating interfaced with (a) buffered DI water and (b) drinking water. Normalized current response from chronoamperometry experiments at potential values that gave peak current for (c) buffered DI water and (d) drinking water.

increased, but the peak current slightly shifted from −0.35 V at low concentrations to −0.45 V at high concentrations.

PFAEI-coated platinum was downselected to be a promising working electrode for PFOA sensing. Figure 2d plots with normalized current response from SWV experiments with a platinum wire working electrode with and without PFAEI coatings as a function of the PFOA concentration in solution. The working electrode potential values for the normalized current measurements were −0.40 V versus Ag/AgCl. Figure 2d shows a commensurate current response with increasing PFOA concentration for the platinum working electrode with a PFAEI coating. Conversely, the working electrode wire with no PFAEI coating experienced a slight decrease in the current response when increasing the PFOA concentration in solution. Figure 2d demonstrates the viability of the PFAEI as an effective coating for sensing PFOA with platinum.

In the final experiments with a working electrode wire in a three-point setup, other interfering anions (e.g., nitrate, phosphate, and sulfate), added as potassium salts, were added to the liquid solution matrix with PFOA and without PFOA to test how these interfering anions affect the PFOA sensing. Figure 2e provides the normalized current response with platinum-coated PFAEI working electrodes for three liquid samples of varying PFOA concentrations and mixed with 50 μM of interfering anions from potassium salts. These experiments were performed with chronoamperometry, and the current was analyzed at −0.47 V versus Ag/AgCl. In the presence of nitrate, sulfate, and phosphate anions, the normalized current response got larger with increasing PFOA concentration. Hence, the platinum wire-coated PFAEI is a promising candidate for PFOA detection in aqueous solutions with phosphate, sulfate, and nitrate salts. These initial experiments motivated planar, single-substrate sensor studies for PFOA detection in buffered DI water and drinking water.

With an appropriate coating and metal electrode identified, SPEs with PFAEI coatings were prepared and assessed for PFOA sensing in DI water with sodium perchlorate/perchloric acid and drinking water using SWV (Figure 3a,b, respectively). To make the plots clear, SWV traces for a few PFOA concentrations and a solution with no PFOA are only presented. Figure 3c,d shows the normalized current response for the SPE with PFAEI coating with various PFOA concentrations in buffered DI water and drinking water, respectively. Notably, PFOA concentrations were sensed in both buffered DI water and drinking water at concentrations as low as 15 nM PFOA with the Pine SPE coated with the PFAEI.

The 15 nM detection limit achieved in this work is about 2 orders of magnitude higher than the EPA health advisory level (0.14 nM) and is roughly 10 times higher than the total allowed PFAS concentration limit in drinking water recommended from the European Health Commission.[41] Although the electrochemical sensor reported in this work does not rival the state-of-the-art for LOD in synthetic and actual water solutions, it is a direct method that does not require the addition of redox active probes.[33] We envision further improvements in LOD by optimizing the PFAEI coating thickness with molecular control using the Langmuir Blodgett technique[42] and the use of nanostructured platinum[43] on the working electrode for enhancing the surface area for adsorption.[43]

In summary, a judiciously selected ionomer coating, PFAEI, with commercially available SPEs was developed to sense PFOA in model and actual drinking water samples as low as 15 nM. One potential limitation of the work/technology is the requirement of an optimal acidic pH, ~1.5, to ensure that PFOA remains neutral for adsorption onto the PFAEI while also ensuring a large enough proton concentration exists to minimize the ohmic losses and to promote the HER. The pK$_A$ value of perfluoro-alkyl substances can range from <1 to

−3.[44,45] Future work will focus on improving the electrochemical sensor with the PFAEI by increasing the wire electrode surface area through an alternative circuit design and incorporation of high-surface area, nanoscale platinum electrocatalysts and by optimizing the PFAEI thickness. Additionally, a sensor that can operate robustly without the need of any additional chemicals, such as buffering agents, will also be pursued.

EXPERIMENTAL SECTION

Materials. Stock materials and purities are provided in the Supporting Information.

Preparation of Ionomer-Coated SPEs for PFOA Detection. Ceramic SPEs with platinum working (3.14 mm^2) and counter electrodes and a silver−silver chloride reference electrode (Ag/AgCl) were acquired from Pine Research. The ionomer [3 wt % in a mixture of isopropanol (IPA) and N,N-dimethylacetamide (DMAC)] was drop-casted on the SPE followed by drying at room temperature and removing the solvent further by vacuum drying for 5 min at room temperature. Thickness of the ionomer coated on the substrate was determined via ellipsometry and was about 50−70 nm.

Preparation of PF-AEI-Coated Wire Electrodes for PFOA Detection. Pt metal wire electrodes (OD = 0.5 mm; approximate total surface area = 0.58 cm^2) were submerged in solution of 3 wt % ionomer in a mixture of IPA and DMAc for 3 min followed by vacuum drying for 5 min to obtain PFAEI-coated metal wire electrodes.

Electrochemical Sensing Experiments with Wire Electrodes. A potentiostat/galvanostat, Gamry Instruments 1010E, was employed for SWV and chronoamperometry experiments. PFOA sensing was demonstrated using a three-electrode configuration, with a platinum wire serving as a working electrode, a platinum counter electrode, and a Ag/AgCl reference electrode. 7.69 mM PFOA analyte stock solution was prepared in DI water. The electrolyte solution (10 mL) containing 70 mM HClO$_4$ and 33 mM NaOH of pH 1.5 was titrated with 0−132 μL of PFOA stock solution (7.69 mM) to obtain the desired final PFOA concentration in the range of 0.77−100 μM at pH ∼ 1.5 before measuring the current responses using voltammetry and chronoamperometry techniques. All experiments used supporting electrolyte containing 70 mM HClO$_4$ and 33 mM NaOH with PFOA in a concentration range of 0.76−100 μM at pH ∼ 1.5. The normalized current response $i/i*$ is used to represent the sensor response versus PFOA concentration (note: $i*$ is the current response with no PFOA present in the solution). The chronoamperometry measurements were performed in the same concentration range by applying a cathodic step potential of −0.47 V versus Ag/AgCl for the platinum wire coated with the PFAEI for a period of 60 s.

Electrochemical Sensing Experiments with SPEs. SWV was carried out on the Pine SPEs immersed into the solution that contained PFOA of varying concentrations in the range from 0 to 500 nM. A supporting electrolyte matrix before the addition of PFOA contained perchloric acid (HClO$_4$) at 70 mM and sodium hydroxide at 33 mM. This resulted in a solution pH of 1.5. All SWV experiments are conducted in the potential window from 0 to −1.0 V versus the Ag/AgCl reference electrode using a 50 mV amplitude, a potential step of 0.75 mV, and a frequency of 25 Hz. Mild stirring was applied during the SWV experiments. Chronoamperometry measurements were performed by applying a cathodic step potential of −0.76 V on SPEs for a period of 60 s. The cathodic peak potential in different experiments was determined from voltammetry measurements.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05847.

> Details of chemicals and materials used, including purity of electrode materials; chemical structures of ionomer coatings; and pH-dependent sensor responses (PDF)

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Notes

The authors declare the following competing financial interest(s): A provisional patent application has been filed on this work at Louisiana State University (LSU).

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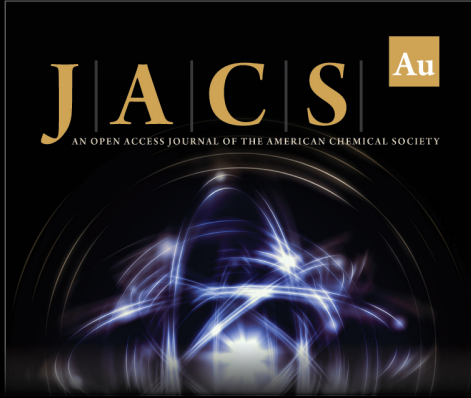
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