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Electrochemical response of titania, zirconia, and alumina electrodes to phosphate adsorption

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ABSTRACT

Low-range (nanomolar), on-site sensing of phosphate concentrations in water is yet to be available, as current methods trade off sensitivity for processing time. To aid in the development of an electrochemical phosphate sensor that satisfies these needs, metal oxides were tested for sensitivity to the phosphate analyte. Titania (TiO_2), zirconia (ZrO_2) and alumina (γ-Al_2O_3) coated electrodes produced via sol–gel methods were compared as sensing materials for this purpose, as these materials strongly adsorb phosphate. Perturbations of cyclic voltammograms and electrochemical impedance spectra indicated the effects of phosphate addition over the pH range of 6.00–8.75. Potential cycling of the titania and zirconia electrodes produced cathodic features that showed competition between the phosphate ion and OH^-. Both lower pH and greater phosphate concentrations increased capacitance for all metal oxides tested. Titania and zirconia electrodes produced a lin–log relationship between the phase of impedance and phosphate concentration, and the relationship proved to be definitive for the porous titania electrodes over the full pH range tested. Titania also showed lesser memory effects with respect to the signal coming from phosphate adsorption than did that of zirconia. Overall, the titania-coated electrode is better poised for purposes of developing a sensor for phosphate.

1. Introduction

In the 1970s, Shindler showed phosphorus to be a limiting nutrient for algal growth in large-scale lake experiments [1]. Under environmental pH conditions, the most easily metabolized forms of phosphorus by cells are the inorganic orthophosphates, primarily HPO_4^{2-} and $H_2PO_4^-$. In the U.S., recommended levels for phosphate levels in lakes are less than 0.05 ppm as P [2], corresponding to 1.6 μmol dm^{-3} phosphate. However, healthy lake water phosphate concentrations are possibly at nanomolar (10^{-9} mol dm^{-3}) levels [3]. Thus, practical, real-time, in situ monitoring of water that is not highly eutrophic would require a sensor that can measure submicromolar phosphate concentrations. Unfortunately, a sensitive phosphate sensor for these real-world applications does not yet exist. Generally, phosphate concentrations are determined via reagent-based colorimetric methods with a UV–visible spectrophotometer, in a laborious process that normally takes place away from the water source. Portable commercial colorimetric phosphate sensors have been developed, with detection limits 0.05–0.10 mg L^{-1} P as phosphate (1.6–3.2 μmol dm^{-3}) [4]. More sensitive colorimetric phosphate detection methods [5–11] may be impractical for common use in real water samples due to bulky equipment and long wait times for chemical equilibrium to be established with the reagent. Electrochemical techniques, most of them based on voltammetry, have been also tried and summarized elsewhere [12]. Their detection limits are in the micromolar level. An amperometric biosensor has been shown to detect submicromolar phosphate [13], but would have limited applications in natural waters as its environment needs to be buffered to prevent degrading the enzyme coating.

Phosphate specifically adsorbs to metal oxides, hydroxides, and oxyhydroxides (collectively called metal (hydr)oxides) at the oxide–aqueous solution interface in the electric double layer. Specifically, inner-sphere adsorption of phosphate onto these minerals changes surface electrochemistry. On these (hydr)oxides, the phosphate anion can be considered potential-determining, as the electrochemical properties of the oxide surfaces are chemically modified by phosphate adsorption. These features could be detected with a potentiostat, as long as the signal, given by the contact area between the electrolyte and the (hydr)oxide, is large enough. Nanoporous materials produced via sol–gel methods can yield a high specific surface area, sometimes hundreds of m^2 per gram. With this large exposure of a mineral surface to the analyte, capacitive effects of ion adsorption into the electrical double layer of an electrode may be amplified. Using an electrode with a nanoporous hematite (α-Fe_2O_3) coating, submicromolar phosphate concentrations caused measurable perturbations in results

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from cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) over a range of circumneutral pH [14,15]. As metal oxides strongly bind phosphate, we have investigated the voltammetric and impedance response of additional oxide (TiO_2, ZrO_2, and γ-Al_2O_3) coated electrodes immersed in aqueous solutions of phosphate at pH values commonly found in natural waters. This study is intended to evaluate the potential of these oxides to provide an identifiable and repeatable signal in an interference-free medium. As an electrochemical sensor should have high sensitivity to the analyte, applicability over a range of pH, and negligible hysteresis of measurement, we investigated these issues in order to judge the potential of these metal oxide coated electrodes for electrochemical phosphate sensing.

2. Materials and methods

2.1. Electrode preparation

Titania (TiO_2) sols were produced in a method detailed by Xu and Anderson [16]. A 1:12 dilute aqueous solution of titanium isopropoxide, $Ti(OPr^i)_4$ (Aldrich), was acidified with concentrated HNO_3, and the precipitates were stirred for three days at room temperature until peptized into a stable suspension. A portion of the colloidal suspension was dialyzed twice in 18 MΩ cm H_2O, and the solution was then passed through a 0.45 μm filter membrane to allow only nanoparticulate colloids in the final suspension (sol). The titania sol had a final density of 20.0 g L^{-1} with a pH of 3.6. TiO_2 particles were found to have mean diameter 27.1 nm (Malvern Zetasizer). Zirconia (ZrO_2) sols were made with HNO_3 acidified and peptized 1:15 dilute aqueous zirconium propoxide, $Zr(OPr^n)_4$ (Gelest, Inc.) and purified using the same method used to prepare the titania sol. This method produced zirconia sols at pH 2.3 with particulate density of 14 g L^{-1} and mean particle size of 40 nm. Both sols were stored in glass bottles at room temperature.

An alumina (AlOOH) sol was produced from aluminum tri-sec-butoxide, ATSB (Gelest, Inc.), in a method adapted from Anderson et al. [17], in which 121 mL of ATSB were diluted with 129 mL 2-butanol, and the mixture added to 1036 mL of 80 °C heated ultrapure water and stirred for 1–2 h. The stirred solution was acidified with 22.7 mL of 1.6 mol dm^{-3} HNO_3, and 2-butanol was evaporated from the resulting suspension by mixing at 80 °C for 4 h. The remaining colloidal solution was refluxed for 12 h, then allowed to cool and passed through: (1) a Type A/E glass fiber filter, (2) a 8 μm filter membrane, and (3) a 0.45 μm filter membrane. The final sol had a pH of 3.7, with density of 34.5 g dm^{-3} and mean particle size 26 nm. The sol was stored in a glass bottle at room temperature.

Coated electrode materials were prepared by dip-coating 1.0 cm × 5.0 cm × 0.5 mm segments of conductive 99.0% nickel (Ni) foil with titania, zirconia, or alumina sols followed by thermal treatment. Prior to coating, the Ni foil was conditioned by sanding, acid washing and heating as described in an earlier work [14]. Upon cooling, the supports were dip-coated by placement into and subsequent withdrawal from the sol at 5.0 mm s^{-1}. The electrode was then allowed to air dry. Electrodes with zirconia and alumina coatings were dipped and dried five and ten times, respectively. The xerogel film was fired at 500 °C for 10 h to sinter the porous metal oxide ceramic coating onto the substrate. The pore size distribution and specific surface area of ceramics fired at these temperatures and times were determined from the N_2 adsorption isotherms at 77 K using a Micromeritics ASAP 2010 analyzer. Electrode surfaces were examined with a scanning electron microscope (SEM) on a LEO 1530 FESEM.

2.2. Chemicals

Phosphate solutions were prepared in a sodium perchlorate electrolyte: $NaClO_4 \cdot xH_2O$ (99.99% trace-metal free) ionic strength buffer to achieve a concentration of 5×10^{-3} mol dm^{-3}. Sodium phosphate was added to this buffer solution to achieve phosphate concentrations in the range of 10^{-8} to 10^{-4} mol dm^{-3}. Between electrochemical measurements obtained at each phosphate concentration, solutions were titrated in 0.25 pH unit increments between pH 6.00 and 8.75 with microliter quantities of 0.1 mol dm^{-3} solutions of ACS analytical grade NaOH and $HClO_4$. Due to the contribution of the phosphate ion, 10^{-4} M phosphate increased the ionic strength somewhat over the background electrolyte; the effect is an ionic strength increase of 2.2% at pH 6 and 5.0% at pH 8.75. Ionic strength was increased by less than 1% for phosphate concentrations of 10^{-5} mol dm^{-3} and lower. A set of blank solutions made with 5×10^{-3} mol dm^{-3} $NaClO_4$ was prepared and pH-adjusted for performing similar experiments to those performed with phosphate-containing dilutions.

2.3. Apparatus and electroanalytical procedure

The electroanalytical protocol was similar to the one used in a previous study of the effects of pH and phosphate concentration on the electrochemical response of a hematite electrode [15]. Briefly, a three electrode electrochemical apparatus consisted of the thin-film working electrode, a saturated calomel reference electrode (SCE) placed 5 mm away from the working electrode, and a platinum counter electrode that completed the circuit in 250 mL of blank or phosphate-containing electrolyte solution in a pre-cleaned glass container. The experiments were kept in an illuminated environment at 22 °C. CV and EIS techniques utilized a Princeton Applied Research VMP2-Z potentiostat with starting parameter inputs and data analysis using BioLogic EC-Lab V10.18 software. The resulting EIS data were obtained as the impedance magnitude ($|Z|$) and phase angle (θ) for each frequency sampled.

With the purpose of obtaining consistent readings [14], the electrodes were pre-scanned 200 times at the rate 150 mV s^{-1} over the electric potential window −0.3 to 0.8 V vs. SCE. The system was left at rest for 2 min to return to the open circuit potential then was cyclically scanned five times with a 150 mV s^{-1} scan rate over −0.3 to 0.8 V vs. SCE, with output saved from the fifth scan. For the EIS phase of the experiment, the potential was first held at −0.24 V vs. SCE for 3 min. Next, an alternating sinusoidal potential of ±20 mV peak-to-peak was applied over a bias potential of −0.24 V vs. SCE. The recorded frequency range for this sinusoidal potential application was 10 kHz–0.05 Hz. After performing the CV and EIS measurements of a pH 6.00 solution, the pH was titrated upward 0.25 units with 0.1 M NaOH with the sample again undergoing five CV cycles and one electrochemical impedance scan over the frequency range. These steps were repeated until measurements reached a final pH of 8.75. This procedure was used to measure CV and EIS response of solutions with phosphate concentrations of 0, 10^{-8}, 10^{-7}, 10^{-6}, 10^{-5}, and 10^{-4} mol dm^{-3}. Memory effects for the titania and zirconia electrodes in phosphate were analyzed by EIS measurements. These were made in 250 mL solutions of phosphate in 5×10^{-3} mol dm^{-3} $NaClO_4$ electrolyte titrated to pH 8.50. Phosphate solutions were 10^{-9} to 10^{-6} mol dm^{-3} in half-log concentration units, and five potential cycles over −0.3 to 0.8 V vs. SCE between each concentration measurement were measured. After performing the test at 10^{-6} mol dm^{-3} the electrodes were placed and re-tested in a 250 mL beaker of 5×10^{-3} mol dm^{-3} $NaClO_4$, pH 8.50. The resultant phase angle (θ) at the chosen frequency was compared to the standard curve for a measure of recovery of pristine electrochemical signal.