

Letter

In Situ Electrochemical Dilatometry of Phosphate Anion Electrosorption

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Supporting Information

ABSTRACT: Here we investigate the competitive electrosorption of mono- and divalent phosphate anions through electrochemical desalination- and dilatometry-based experiments. Through in situ dilatometry, we monitor the strain at the electrode surface as anions and cations are electrosorbed. Strain measurements show that the presence of divalent ions promotes a greater than anticipated electrode expansion during cation (Na⁺) electrosorption. The expansion observed with Na⁺ equaled the expansion observed with HPO₄²⁻. Because the ionic radius of Na⁺ is smaller than that of HPO₄²⁻, the symmetric expansion suggests that divalent anions do not completely desorb during electrode regener-



ation, causing the adverse interactions with the cation during co-ion expulsion. This results in a decrease in desalination performance, indicated by a decreased salt adsorption capacity. Conversely, an expected asymmetric expansion during anion and cation electrosorption occurs with monovalent phosphate anions $(H_2PO_4^-)$, indicating that monovalent ions can be effectively replaced by the cation at the electrode surface.

INTRODUCTION

Ion separation processes are critical for many industrial, municipal, and environmental applications.¹ Separation processes require the use of physical (membranes) or masstransfer-based operations (distillation, absorption, and adsorption).² Mass transport operations have a high energy demand and typically require chemical-based regeneration, whereas physical operations are low energy but foul and are not intrinsically selective. Electrochemically driven separations (capacitive deionization, electrochemically modulated liquid chromatography, and battery deionization) have demonstrated new avenues for achieving low-energy ion removal and are electrochemically regenerated without the need for chemicals.³ Furthermore, these approaches are beginning to achieve selectivity through the use of electrochemical redox-responsive receptors.^{4,5}

Gaining molecular level insight into water–electrode interfaces is an important next step needed to answer questions related to the energetics and selectivity of electrosorption.^{5–7} Fundamental knowledge is needed regarding both the static and dynamic nature of the electric double layer (EDL) and interface during separation. This is critical for understanding the rate-limiting mechanism associated with electrosorption (adsorption and desorption) under environmentally relevant conditions. While in simple systems with model constituents

(monovalent salts) adsorption and desorption occur at equal rates, in systems with more complex constituents (salts with varying degrees of valence and hydration) competitive adsorption between species can alter the salt removal process.⁸ One of the most common constituents to which this applies is phosphate anions, which are well-known to exist in monovalent (H₂PO₄⁻) and divalent (HPO₄²⁻) states depending on the pH of the feed source.^{9–12} Because of the potential environmental and economic considerations associated with the recovery of phosphorus from waste streams, developing ways to recover and concentrate phosphate anions is becoming more important.^{13–15}

Here, we investigate the dynamics of phosphate anion electrosorption processes using electrochemical dilatometry^{16,17}, desalination testing^{18,19} and through a theoretical analysis.²⁰ Dilatometry experiments probe the phosphate anion interactions at the electrified interface by measuring changes in the electrode strain during cyclic voltammetry experiments. Strain measurements are also correlated with desalination- and electrochemical-based characterization. The results discussed

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here show increased strain in electrodes with divalent phosphate anions (HPO₄²⁻) during co-ion expulsion (negative polarization). Strain is associated with an ion's inability to adsorb to the electrode surface or be transported through nonporous regions. In contrast, this mechanical strain is not observed for monovalent phosphate anions $(H_2PO_4^{-})$. Ineffective desorption of bulky anions may be a contributing factor leading to lower desalination performance and salt adsorption capacity. These interactions may also promote a degree of selectivity associated with larger ionic radii and charged species. Prior batch desalination results have suggested that divalent phosphate anions may accumulate more readily at the surface because of the energetic advantage associated with screening the surface charge.²¹ This work presents an additional explanation related to the unfavorable chemomechanics associated with the co-ion expulsion of divalent phosphate anions. Increased strain is observed in the electrode during divalent desorption processes and may contribute to the observed selectivity of divalent phosphate anions over monovalent species. Understanding and measuring competitive electrosorption-based processes are imperative for the separation of complex waste streams.

MATERIALS AND METHODS

Preparation of the Electrode. The activated carbon electrode was prepared by dispersing YP-50F activated carbon (Sanwa Components International Inc.), carbon black (Sigma-Aldrich), and polytetrafluoroethylene (60% weight dispersion, Sigma-Aldrich) in a 90:5:5 ratio by weight in ethanol (Fisher Scientific). The mixture was stirred constantly and dried on a hot plate stirrer (Fisher-Scientific), until a desired consistency was reached. After the mixture was dried, the carbon slurry was rolled onto a graphite sheet (Alfa-Aesar) using a roller to a thickness of 0.4 mm. Two electrodes with diameters of 10 mm were cut out and used for the tests as working and counter electrodes. The weight of the electrode was 20 ± 2 mg.

Electrochemical Dilatometry. An ECD-nano-DL Dilatometer from EL-Cell (Germany) with gold current collectors was used for in situ electrosorption experiments. Three-electrode electrochemical and dilatometric measurements were performed at 22 ± 1 °C with a Biologic VSP-300 potentiostat. The electrochemical cell contained an oversized counter electrode with a mass that was at least 20 times the mass of the working electrode. The vertical deformation during anodic and cathodic scans was measured with an accuracy of approximately 15 nm and normalized to the electrode thickness at the point of zero strain.

Desalination Testing. The desalination system was comprised of a flow cell with a projected area A_{cell} of 25 cm². The feed chamber consisted of a polycarbonate flow channel with a thickness of 0.47 cm. Electrodes were placed on graphite sheets that were placed on gold-plated copper current collectors. The feed flows vertically through the center of the cell. A cation (CEM) and anion exchange membrane (AEM) separated the feed from the electrode (Selemion AMV/CMV, Chiba, Japan).

RESULTS AND DISCUSSION

The degree of desalination from a capacitive deionization cell was conducted in both continuous (Figure 1a) and batch mode (Figure S2) experiments. In both series of experiments, phosphate aqueous solutions with a lower pH (\approx 4) resulted in



Figure 1. (a) Effect of pH on the effluent concentration and (b) theoretically predicted effect of valence on ion removal.

a faster rate of salt removal and greater total salt removed $(\Delta C/C_0)$ for each cycle. For the continuous mode desalination-based testing, the energy consumption for the pH 4 electrolyte was 0.03 kWh/mol, whereas the pH 9 phosphate electrolyte resulted in an increase in energy consumption to 0.09 kWh/mol. Because of the pK_a of the solution, during tests conducted in pH 4 electrolytes, H₂PO₄⁻ was the dominant anion. In addition, during tests in pH 9 electrolytes, the dominant anion was HPO_4^{2-} . The increase in energy consumption ascribed to the presence of divalent ions also resulted in a decrease in the energy normalized per adsorbed salt (ENAS) from 8.3 μ mol/J (pH 4) to 3.2 μ mol/J (pH 9). Note that the ENAS values for the phosphate anions is 2-4 times lower than the ENAS values reported with sodium chloride.²² This is due to an increase in the ionic radius of the phosphate anion (≥ 0.302 nm hydrated ionic radius) compared to that of chloride (0.195 nm hydrated ionic radius). Because of the size of the desalination systems, batch mode experiments provided further insight into the potential for anion removal (Figure S2). Here, the energy consumption (kilowatt hours per mole) again was 2 times greater for pH 9 solutions (divalent anions) than for pH 4 solutions (monovalent). In all of the tests, an increase in current was observed with the pH 9 solution, which was attributed to the higher conductivity (Figures S1 and S2).

The experiments are consistent with Gouy–Chapman– Stern theory, which predicts salt removal dynamics within an electric double layer (Figure 1b).^{20,23} In aqueous solutions, the electric double layer (EDL) is comprised of the Stern layer that has oppositely charged counterions attracted to the surface and a diffuse layer that has a mix of counterions and co-ions. The length at which the diffuse layer disperses into the medium, otherwise known as the Debye length (λ_D), varies inversely with the electron valence, resulting in less disperse EDLs when di- or trivalent ions are present. The Debye length is important (a)

0.10

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(b)

0.10

0.8

Figure 2. Dilatometry experiments detailing the relative height change experienced by the electrode during a cyclic voltammogram conducted in (a) pH 4 and (b) pH 9 phosphate-based electrolytes. Relative height change recorded at various scan rates in (c) pH 4 and (d) pH 9 phosphatebased electrolytes.



Figure 3. Electrode relative height change in (a) pH 4 and (b) pH 9 phosphate electrolytes as a function of normalized time.

for determining the electric potential of the double layer and is incorporated into a transient model. Through the introduction of valence into the model, the result predicts a decrease in the level of salt removal with an increase in valence (Figure 1b).

During the dilatometry experiment, the voltage of the whole cell was varied by performing cyclic voltammetry. The associated relative height change experienced by the cell ranged from 0 to $\sim 1\%$ depending on whether the anion or cation was being electrosorbed on the carbon film electrode (Figure 2a,b). Each cyclic voltammogram demonstrates a pseudorectangular shape at 2 mV/s (slow scan rate) that is typical of electrode systems. The specific capacitance values for the pH 4 and 9 electrolytes in a three-electrode configuration are 38 and 40 F/g (Figure S3). The low capacitance is attributed to the transport limitations associated

with phosphate anions in the micropores. Evidence of high tortuosity can be observed at the potential boundaries of the cyclic voltammograms. In a highly accessible electrode, the current is independent of voltage (vertical line) at the voltage boundaries.^{19,20,24} However, in these electrolytes, there is a slight dependence of voltage on the current density at the voltage limits. Subsequently, as the potential swings into the positive region, a large expansion is observed in the pH 4 and 9 electrolyte systems. The large expansion is associated with bulky anion (monovalent and divalent phosphate) adsorption. The electrode expansion or strain is reversible for each successive cycle. Large expansions are observed during the positive polarization of the electrode in the acidic electrolyte with a monovalent phosphate anion $(H_2PO_4^{-})$, and less expansion is observed when the electrode is polarized in the negative region. The anisometric charge-dependent swelling of the porous carbon is well documented for non-aqueous and ionic liquid electrolytes characterized by bulky cations.²⁵

The assymmetric expansion behavior indicates that the carbon experiences more strain during phosphate electroadsorption processes than during Na⁺ electroadsorption processes (Figure 2c). In contrast, the expansion process is more symmetric between positive and negative polarization swings for the basic electrolyte that contains divalent phosphate anions (HPO_4^{2-}) (Figure 2d). This result is counterintuitive because both electrolyte systems have the same cation, which suggests that there is some interaction between the divalent phosphate anion (HPO_4^{2-}) and cation during negative polarization. When the electrode switches from positive to negative polarization regimes, the anion is expelled from the surface and replaced with a cation. During this switch, co-ion expulsion dynamics can play a role in the electric double-layer structure and impact the efficiency of the electroadsorption processes. Furthermore, this interaction may be amplified for the divalent phosphate anion, because two sodium ions are required to maintain charge neutrality at the surface during the potential reversal. Thus, the symmetric expansion observed in the basic electrolyte may occur because of a complex desorption mechanism associated with the dual charged phosphate anion. The rate of the electrode expansion process decreases with scan rate (Figure 2c,d) for both electrolytes (mono- and divalent anions). The decrease in electrode expansion is a signal that ions are not reaching the adsorption equilibrium because of transport limitations in the microporous region of the electrode.

The dissimilar strain or expansion properties of the monovalent and divalent phosphate anions are more obvious when multiple cycles are presented with respect to normalized time (Figure 3a,b). The asymmetric expansion profile for the monovalent phosphate anion is readily apparent at 2 mV/s through the presence of repeating units of small and large peaks. However, little to no expansion is observed at scan rates of greater than 10 mV/s (small peaks are completely suppressed). This is not surprising, as at higher scan rates, ionic access to the interface is limited. In contrast, significant expansion occurs in the electrolyte with the divalent phosphate anion at scan rates of greater than 20 mV/s. The symmetry in expansion does decrease with an increase in scan rate (divalent phosphate anion) but is still readily apparent indicating that the co-ion expulsion mechanism is not dependent on the kinetics of the charging process. Insight into the chemomechanics of these complex anions provides a potential explanation for the recent experimental results of Huang et al., which demonstrated preferential electroadsorption selectivity of Cl⁻ over H₂PO₄⁻ and HPO₄²⁻ over Cl^{-,9} Prior results have suggested that there is a preferential adsorption and accumulation of divalent phosphate anions in the double layers because there is an energetic advantage of screening the surface charge with a negative two charge anion.²¹ Our work extends this finding by demonstrating that there are also chemomechanical considerations at play during the co-ion expulsion processes of divalent phosphate anions that do not exist for monovalent phosphate anions.

Molecular insight into fundamental interactions that occur at relevant solid—water interfaces for water treatment, remediation, and desalination applications is important for engineering next-generation materials. Electric field and electrochemical systems are being increasingly investigated in water technologies as a means of mitigating degradation (fouling), informing system performance (sensors), and improving selectivity. This work investigates the fundamental nature of electroadsorption processes for relevant water contaminants and provides insight into the origin of decreased ion separation properties for dual charged phosphate anions in comparison to single charged phosphate anions. Designing materials that can exploit these mechanisms may provide a means for engineering future systems with selectivity. Here we highlight the complexity associated with field-assisted separations in water applications where species with varying degrees of hydration and valence are present. Furthermore, we highlight how competitive electrosorption can be captured in various dynamic environments using dilatometry and theory to ultimately explain results obtained through desalination-based testing.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.es-tlett.8b00542.

Experimental procedures and calculations for ex situ characterization, materials and methods, and the theoretical framework (PDF)

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Notes

The authors declare no competing financial interest.

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