



Effect of the electronegativity on the electrosorption selectivity of anions during capacitive deionization

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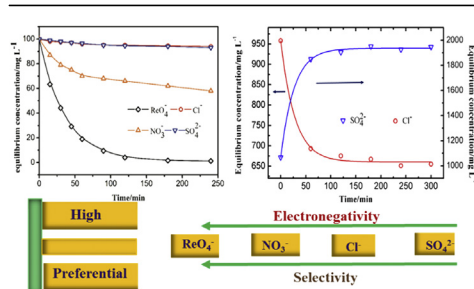
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HIGHLIGHTS

- Combined chemical thermodynamics and classic Stern's theory derives expression.
- Expressions given for describing electronegativity dependent ion selectivity.
- Anions with a large electronegativity exhibit high selectivity.
- The adsorption capacity shows a logarithmic relation with the anode potential.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 28 August 2017

Received in revised form

14 November 2017

Accepted 6 December 2017

Available online 7 December 2017

Handling Editor: E. Brillias

Keywords:

Capacitive deionization

Electronegativity

Electrosorption

Selectivity

Desalination

ABSTRACT

The effect of electronegativity on the electrosorption selectivity of anions during capacitive deionization was investigated via a combination of experimental and theoretical studies. A model was developed based on chemical thermodynamics and the classic Stern's model to reveal the role of the anode potential and to describe electrosorption selectivity behavior during capacitive deionization. The effects of the anode potential on the adsorption of Cl^- and ReO_4^- were studied and the obtained data were used to validate the model. Using the validated model, the effects of the anode potential and electronegativity of various anions, including Cl^- , ReO_4^- , SO_4^{2-} and NO_3^- were assessed. The experimental results for the electrosorption of Cl^- and ReO_4^- corresponded well with the developed model. The electrosorption capacity demonstrates a logarithmic relationship with the anode potential. The model showed that the electronegativity significantly affects the selectivity. In a mixed Cl^- , ReO_4^- , SO_4^{2-} and NO_3^- solution, ReO_4^- was preferentially adsorbed over the other three anions, and the following selectivity was exhibited: $\text{ReO}_4^- > \text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$. The results showed that the effect of flow rates on the electrosorption selectivity can be considered negligible when the flow rates are higher than 112 mL min^{-1} . The anions selectivity can be further enhanced by increasing the anode potential, and electrosorption selectivity is no appreciable decline after 6 experiments.

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1. Introduction

Water shortages are gradually emerging as a worldwide problem due to environmental pollution and accelerating population

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growth, leading to crisis related to food production and public health issues in more and more regions. Accordingly, recent studies have developed a large variety of treatment technologies for the removal of pollutants from waste streams and contaminated water (Ayranci and Conway, 2001; Zou et al., 2008).

Of major interest, capacitive deionization (CDI), particularly by utilization of activated carbon, is recognized as a potential technique for large-scale wastewater purification because it is energy-saving, and there is no need for a high-pressure pump and membrane or generation of secondary waste (Tang et al., 2016a,b). In the electrosorption process, when an electrical potential is applied to electrodes, charged ions migrate to the electrodes and are electrostatically separated from aqueous solutions via the formation of an electrical double-layer (EDL) at the electrode/electrolyte interface (Fan et al., 2017). Therefore, electrical potential and formation of an electrical double-layer are two critical factors for high-performance electrosorption capacity. In current research, the enhancement of the adsorption rate and capacity by electrosorption has received extensive, serious consideration and has been supported by in experiments (Han et al., 2007; Wang et al., 2007; Chen et al., 2011; Park and Kwak, 2014). A 61.0% improvement in the *m*-cresol adsorption capacity on activated carbon fibers was demonstrated by Han et al. (2007), using a polarization potential of 600 mV. Meanwhile, Wang et al. (2007), reported that a 58.9% enhancement of the NaCl adsorption capacity could be effectively achieved using electrochemical polarization. However, there is lack of theoretical expressions for describing the relationship between the electrosorption capacity and the applied voltage. In 1958, Grahame (1958) reported that, in terms of the Boltzmann distribution law, the concentration of ions in the inner Helmholtz region can be expressed as:

$$n^i = Ka_{\pm} \exp\left(\frac{\phi F}{RT}\right) \exp\left(\frac{\psi^i F}{RT}\right) = K' a_{\pm} \exp\left(\frac{\psi^i F}{RT}\right)$$

where n^i is the concentration of ions in the inner Helmholtz region (Essentially, n^i is the surface concentration of specifically adsorbed ions.), K is a constant for a given system, K' is a function of the surface charge, a_{\pm} is the mean activity of the ions, and ψ^i is the electrical potential at an anion site in the inner region. Experiments to verify the equation were performed using a mercury electrode in contact with aqueous solutions of potassium chloride and potassium iodide at 25 °C. The results showed that fit is better for potassium chloride than potassium iodide. Furthermore, there is a very good linear relationship between the potential across the inner region of the double layer and the amount of specifically adsorbed anions that occurs at higher concentrations. Therefore, further research is needed to gain a better understanding of the potential of CDI as a practical water purification technology.

According to the abovementioned mechanism, in the CDI unit, the electrode material is another important parameter for getting high performance of CDI. Therefore, considerable efforts have been focused on the electrode materials (Huang et al., 2017; Yasin et al., 2017). Gaikwad et al (Gaikwad and Balomajumder, 2016a,b), reviewed the current progress of capacitive deionization electrodes prepared from nanoparticle oxides, carbon nanotubes, graphene, carbon nanofibers, and nonporous carbon cloth, showing the excellent electrosorption of nanomaterials. Wang et al. (2016), prepared a high-performance three-dimensional graphene electrode with higher capacitance and lower inner resistance for flow-through deionization capacitors, showing a high salt adsorption capacity. Besides, other carbon materials, such as activated carbons (Hatzell et al., 2014; Largette and Pasquier, 2016; Yasin et al., 2017), mesoporous carbons, carbon aerogels, polymer-coated electrodes (Gaikwad and Balomajumder,

2016a,b) and their composites, have been explored as candidates for CDI electrode materials. In those carbon materials, activated carbon has been widely used in CDI due to the advantages of good mechanical strength, low-cost, good electrical and high electrical conductivity (Oda and Nakagawa, 2003; Gaikwad and Balomajumder, 2017). Yasin et al. (2017), reported the incorporation of zirconia nanofibers with activated carbon as an effective and simple strategy to distinctly enhance the electrosorption capacity and the salt removal efficiency improved from 5.42 to 16.35 mg g⁻¹.

The coexistence of multiple anions is a typical environmental situation. The anions compete with each other in the electrosorption process, leading to different electrosorption capacities and selectivities. However, theoretical and experimental studies of the structure of the EDL suggest that charged interfaces can have different excess adsorptions of different types of ions, which may depend on the valence state of the ions (Chen et al., 2015), initial concentration, hydration ratio (the ratio of the hydrated radius to the ion radius) (Li et al., 2016) and atomic weight (Gabelich et al., 2002); as such, there is no consensus. Gadkaree (Gadkaree et al., 2004) found that the adsorption capacity for larger ions such as NO₃⁻ is lower than that for the smaller Cl⁻ ions. Mossad et al (Mossad and Zou, 2012), reported that the electrosorption capacity of activated carbon follows the order Cl⁻ > SO₄²⁻ > NO₃⁻ due to the difference of initial feed concentrations of ions. Afkhami (2003) showed the NO₃⁻ is exhibited good selectivity than SO₄²⁻ based on the difference of specific adsorption tendencies. More research has focused on the hydrated radius, but many experimental phenomena cannot be explained by the hydrated radius. In addition, Li et al. (2016), reported that multivalent ions adsorb more easily onto an electrode surface, resulting in a higher electrosorption selectivity. Also, Gabelich et al. (2002), showed that the sorption of solutes should obey the following order: SO₄²⁻ > NO₃⁻ > Cl⁻ because of hydrated radius. In contrast, other researchers have demonstrated that in a mixed solution, the carbon materials show a stronger selectivity for monovalent ions (Hou et al., 2008; Tang et al., 2016a,b). Therefore, the key factors affecting the electrosorption selectivity of ions remain unclear.

Previous research has demonstrated that the efficiency of CDI strongly depends on the surface properties of the electrodes, including the surface area, microstructure and size distribution of the pores, chemical functional groups, and adsorption properties. Faradaic reactions between the dissolved impurities and the electrodes also contribute to the separation mechanisms of the electrodes (Xu et al., 2008). For instance, functional groups such as carbonyl and phenolic groups on the carbon electrode can react with ions and form chemical bonds (Yang et al., 2001). Furthermore, the structure of the EDL will be affected. Therefore, there is another factor that affects electrosorption selectivity.

In this work, we develop a model that describes the relationship between the electrosorption capacity and the anode potential in terms of the principles of chemical thermodynamics and the classic Stern's model. The theoretical results are compared to the new experimental data. Additionally, the effects of the model parameters on the electrosorption selectivity are discussed by analyzing the structure of the anions (Cl⁻, ReO₄⁻, SO₄²⁻ and NO₃⁻) and their electrosorption performance. This study enables the prediction of the electrosorption capacity of electrode materials and contributes to identifying ion selectivity in multi-ionic solutions.

2. Experimental section

2.1. Apparatus

A three-dimensional electrode system was adopted in the adsorption/electrosorption investigation and a structure diagram of

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