



Treatment of molybdate solutions by electro dialysis: The effect of pH and current density on ions transport behavior



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ARTICLE INFO

Article history:

Received 10 March 2016

Received in revised form 28 April 2016

Accepted 29 April 2016

Available online 29 April 2016

Keywords:

Molybdate

Anion-exchange membrane

Chronopotentiometry

Membrane-poisoning

Electrodialysis

ABSTRACT

Molybdate conversion coatings are seen as a viable alternative to produce chromate-free coatings. By the coating process, molybdate containing wastewater are generated and electro dialysis could be applied for salts recovery and process water reuse. In fact, the electro dialysis efficiency for these purposes is associated to the ions transport properties through the ion-exchange membranes. In this work the transport behavior of molybdate ions through a HDX200 heterogeneous anion-exchange membrane was studied using the electrochemical characterization technique of chronopotentiometry. The study was carried out with 0.005 M Na_2MoO_4 solutions at different pH values: 4.8, 6.5 and 12.0. Differences in the chronopotentiometric curves shape as well as in the limiting current density and ohmic electrical resistance values were observed and explained with basis on the molybdenum speciation diagram. The obtained results revealed that, according to the solution pH and current density conditions, polynuclear anions can be formed leading to a membrane-poisoning phenomenon, exposing limitations and suitable conditions of using the electro dialysis in the treatment of molybdate wastewater.

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1. Introduction

Molybdate conversion coatings have been reported [1–3] as a promising candidate to replace chromate conversion coatings that are object of strictly environmental restrictions due to the high toxicity of Cr (VI). Once established industrially, the molybdate conversion coating processes will generate molybdate-containing wastewater that need to be treated before its discharge on the environment. In general, chemical precipitation is the traditional method used to treat metal containing wastewater. However, this method originates a metal precipitate that constitutes an environmental and economic drawback to the involved industries due to the need of adequate disposal of this hazardous waste. Along the years, the electrochemical membrane separation process of electro dialysis, which employs ion-exchange membranes, has been described as an alternative method to the treatment of wastewater containing metal ions [4–9]. In this method, two solutions are obtained, one more concentrated and another more diluted than the original one (namely the spent surface treatment baths or the rinse baths). This is particularly interesting, by the surface treatment process point of view, since allows the reuse of the both

obtained solutions. The more diluted solution can be reused in the rinse bath of the process, while the more concentrated one can be applied to replace the chemical constituents of the surface treatment bath. Considering these advantages, this work aims to evaluate the possibility of using the electro dialysis method in the treatment of molybdate wastewater in order to simultaneously achieve desalting and concentration of the feed solution. This assessment was made using the electrochemical characterization technique of chronopotentiometry. Several works [10–17] have already demonstrated that this electrochemical characterization technique is a powerful tool to obtain this kind of information. This technique allows monitoring the transient process occurring close to the ion-exchange membrane, until a new steady state is reached, by measuring the membrane potential drop as a function of time when an electric current density is applied to the system [10,11]. The chronopotentiometry data can be used to obtain current-voltage curves that give important information as the limiting current density and the ohmic electrical resistance [12–17]. Additionally, the chronopotentiometric curves shape can provide valuable information from the secondary effects associated to the concentration polarization phenomenon [10–17]. The study of these ion transport properties enable the discussion about the limitations and suitable conditions of using electro dialysis to the treatment of molybdate wastewater.

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2. Experimental

2.1. Solutions

The study was carried out with 0.005 M $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ solutions at different pH values: 4.8 (1.02 mS cm^{-1}), 6.5 (1.03 mS cm^{-1}) and 12.0 (3.11 mS cm^{-1}). The solutions were prepared as a surrogate of the molybdate conversion coating rinse bath solution by dissolving the salt in distilled and deionized water. Analytical grade reagent was employed. The pH was adjusted with HCl or NaOH.

2.2. Ion-exchange membrane

The anion-exchange membrane used in this work was the HDX200 (supplied by Hidrodex). This is a heterogeneous anion-exchange membrane containing quaternary amines groups as fixed ion-exchange sites and showing an ion-exchange capacity of 1.8 meq/g of dry membrane [17].

2.3. Electrochemical cell and chronopotentiometric measurements

The chronopotentiometric experiments were accomplished using a 150 mL three-compartment cell as shown schematically in Fig. 1. A heterogeneous HDX100 cation-exchange membrane (supplied by Hidrodex) separated the cathodic compartment from the central compartment to minimize the contribution of the OH^- ions generated in the cathode on the anion-exchange membrane measurements. The exposed area of the membrane surface was of 9.62 cm^2 . The potential drop through the membrane was measured by using two reference (Ag/AgCl) electrodes immersed in Luggin capillaries. Moreover, two graphite electrodes were used to impose the current density, which was supplied by a potentiostat/galvanostat (Autolab, PGSTAT302). The membrane potential response to each current density was automatically recorded for 120 s. After that, the diffusion relaxation of the system was allowed and recorded. Current-voltage curves were reconstituted from the steady-state polarization voltage (obtained from the chronopotentiometric curves) corresponding to an applied current density. All the experiments were conducted at room temperature and without stirring. The experiments were accomplished after a membrane equilibration period of at least 24 h with a solution with the same characteristics as the ones used in the experiments.

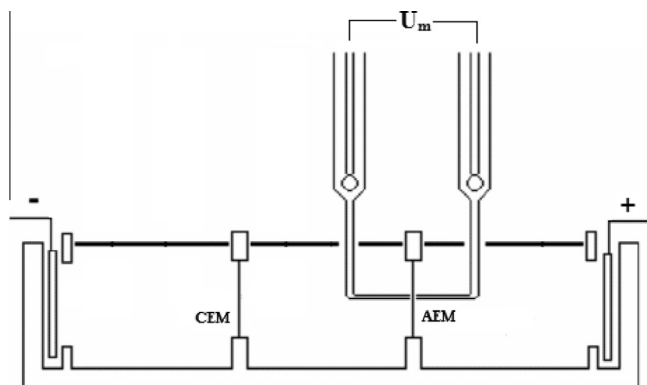


Fig. 1. Schematic diagram of the electrochemical cell used to carry out the chronopotentiometric measurements (CEM: cation-exchange membrane; AEM: anion-exchange membrane; U_m : membrane potential drop).

3. Results and discussion

Fig. 2 shows the current-voltage curve constructed from the chronopotentiometry data obtained for the 0.005 M Na_2MoO_4 pH 6.5 solution.

The three classical electrolyte/ion-exchange membrane current-voltage regions were observed: a quasi-ohmic (region I), where the voltage increases almost linearly with the applied current density, followed by a plateau (region II), which corresponds to the limiting current density and where a sharp increase in the voltage is observed, as a consequence of mass transport polarization (the concentration of ionic species which cross the membrane reach values close to zero on the membrane surface) and finally, a third stage (region III), characterized by a new current density increment, which can be attributed to different phenomena accompanying the concentration polarization and the so-called overlimiting current region [18].

Historically, overlimiting current densities have been linked to the transport of H^+ and OH^- ions formed by the water dissociation ($\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$), resulting in energy consumption without an implication on an additional transport of the salt ions. Besides, additional operational problems, as metal hydroxide scaling on membrane surfaces, can occur due to a local pH change [19]. Thus, electro dialysis classically operates in the ohmic region, below the limiting current density, and the ohmic electrical resistance as well as the limiting current density value are important electro dialysis operational parameters.

The ohmic electrical resistance can be calculated from the inverse of the slope of the ohmic region. The limiting current density can be inferred by the intersection of the two slopes belonging to the ohmic and plateau regions. The obtained values for the 0.005 M Na_2MoO_4 pH 6.5 solution were $588.2 \Omega \text{ cm}^2$ and 0.52 mA cm^{-2} for the ohmic electrical resistance and the limiting current density, respectively.

However, a little evidence of water dissociation in some electrolyte/membrane systems has generated discussions on the topic and other theories have emerged to explain this third current density stage, which cannot be attributed only to the mechanism of water dissociation. Among these theories, those related to convection mechanisms (gravitational convection and electroconvection) can be highlighted [20–22]. These theories are related to a perturbation of the diffusion boundary layer created in the electrolyte/membrane interfaces, leading to an additional flow of salt ions to the membrane surface. Since the current carriers on this third stage

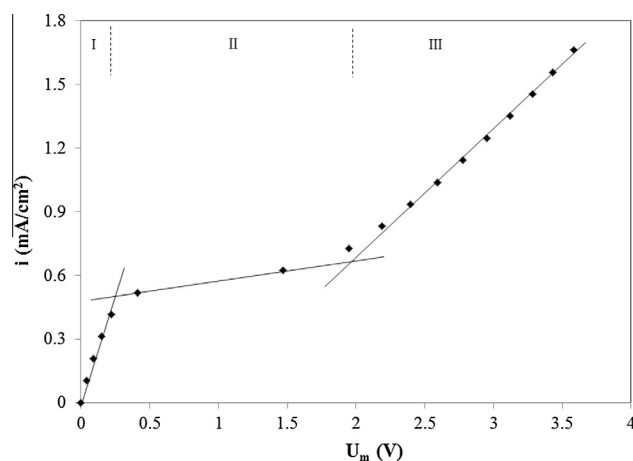


Fig. 2. Current-voltage curve of the HDX200 anion-exchange membrane in contact with a 0.005 M Na_2MoO_4 pH 6.5 solution obtained from the steady-state membrane potential drop of the chronopotentiometric curves.

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