Journal of Membrane Science 453 (2014) 275–281

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Electrodialysis of itaconic acid: A short-cut model quantifying the electrical resistance in the overlimiting current density region

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ARTICLE INFO

Article history:
Received 23 September 2013
Received in revised form
31 October 2013
Accepted 1 November 2013
Available online 20 November 2013

Keywords:
Electrodialysis
Organic acid
Overlimiting current
Modeling

ABSTRACT

Itaconic acid is an anticipated intermediate chemical in the synthesis of biofuels from cellulosic feed stock. Itaconic acid (IA) can be produced by fermentation and continuous fermentation with continuous product removal is highly desired. Electrodialysis with bipolar membranes (EDBM) has this potential and can be used simultaneously for the pH control of the fermenter. EDBM processes for acidification are operated at overlimiting current densities. The resistance of a diffusion boundary layer and consequently mass transfer of the IA through the anion exchange membrane under these conditions are not fully understood yet. To design the process a short cut method is required to describe the current voltage characteristic of the EDBM stack. In a first modeling approach, a differential resistance was assumed to describe the current–voltage behavior of the anion exchange membrane determining the major resistance. Experiments on a single membrane test cell under stationary conditions were carried out to measure *iV* -curves for different bulk phase compositions and IA transfer through the AEM. Special attention was given to the influence of pH and ionic strength. The resistance at overlimiting currents follows an exponential law and it depends on pH and ionic strength only with regards to the absolute level of the current. An approximation is presented for the current voltage characteristics above the limiting current density based on an extended Nernst–Plank model having diffusion coefficients as input parameters for the limiting current densities and a single Schmidt Number for the overlimiting currents at any feed composition. The latter acknowledges the hydrodynamic character of electroconvection as contributor to the overlimiting transport.

1. Introduction and motivation

The motivation to comprehensively understand the mass transport of a bifunctional acid such as itaconic organic acid lies in its potential use as a bio-based intermediate product. Itaconic acid is considered as a platform chemical for novel bio-based synthetic fuels for instance [1,2]. It can be derived from glucose by fermentation using a number of different micro-organisms [3]. As the current state of the art, *Aspergillus terreus* (AT) is employed as bacterium in batch fermentation. With itaconic acid becoming a precursor for biofuels, its demand can be expected to increase significantly. Batch operation will need to be replaced in favor of a continuous process which in turn requires continuous product removal from the fermenter. This change of method involves an exchange of micro-organisms as well.

Ustilago maydis (UM) is supposed to meet the requirements of continuous fermentation [3]. Recently, we presented a new in situ product recovery strategy called Reverse Flow Diafiltration (RFD) [4]. The use of UM during fermentation yields advantages and disadvantages. Its major advantage over AT is its haploid growth [5,6] being beneficial for a continuous process. A potential overall process to turn cellulosic biomass into itaconic acid is shown in Fig. 1.

For isolation and concentration of mono- and multi-functional organic acids such as itaconic acid, ion exchange membranes can be used [7]. In order to integrate product removal and pH control in one unit operation, bipolar membranes are used [8] in a variety of different stack configurations with monopolar membranes. In many cases, the itaconate ions pass an anion exchange membrane and form their respective acid with protons produced by the bipolar membrane.

Fig. 2 shows the transport of ionic species in a typical membrane stack configuration. The transport of the organic acid through the anion exchange membrane shows a high resistance and it is important to quantitatively describe this resistance by a mathematical approximation in order to be able to design the process properly as a function of the ionic solution composition.

In the past, electrodialysis has been used to purify and concentrate other organic acids, e.g. lactic acid [9], formic acid [10] and citric acid [11]. An overview of a broad range of ED and EDBM processes in biorefinery applications is provided in a review

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http://dx.doi.org/10.1016/j.memsci.2013.11.008

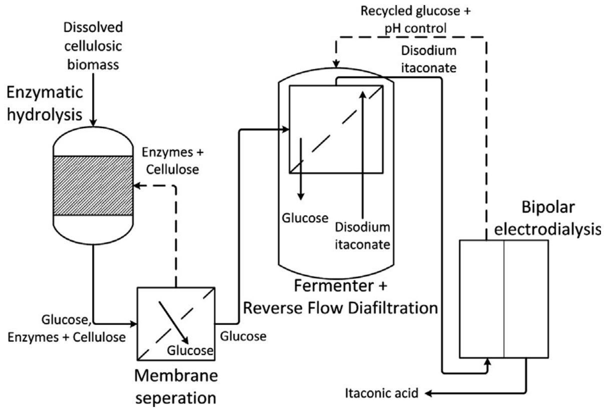

Fig. 1. Process scheme of a continuous production of itaconic acid from cellulosic biomass by enzymatic depolymerization, glucose fermentation and itaconic acid recovery.

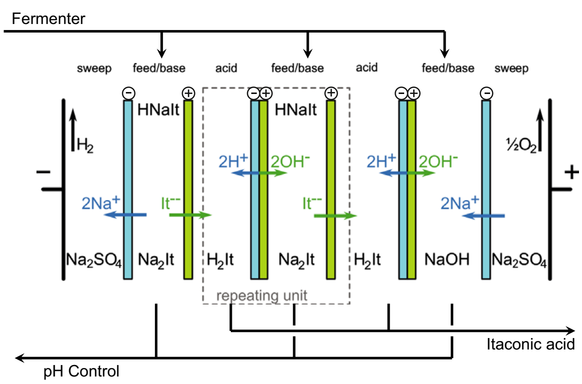

Fig. 2. Membrane stack configuration for the bipolar membrane electrodialysis process recovering itaconic acid and producing NaOH for pH control in the fermentor. The green membranes are AEM, the blue membranes CEM and the green and blue ones are the BPM. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

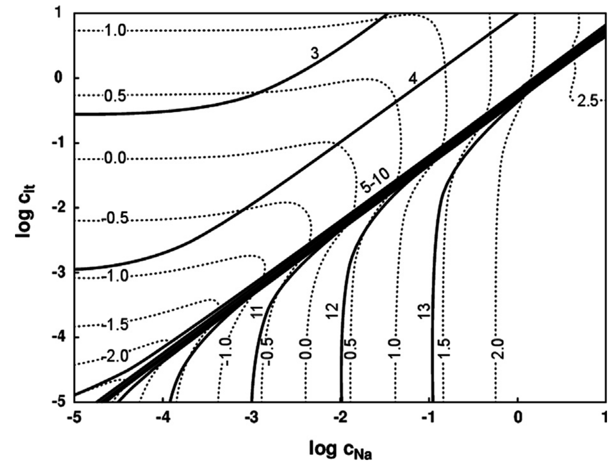

Fig. 3. pH value (solid line, –) and electrical conductivity (dotted line, mS/cm) as functions of the logarithmic concentration of itaconic and sodium ions (mol/L).

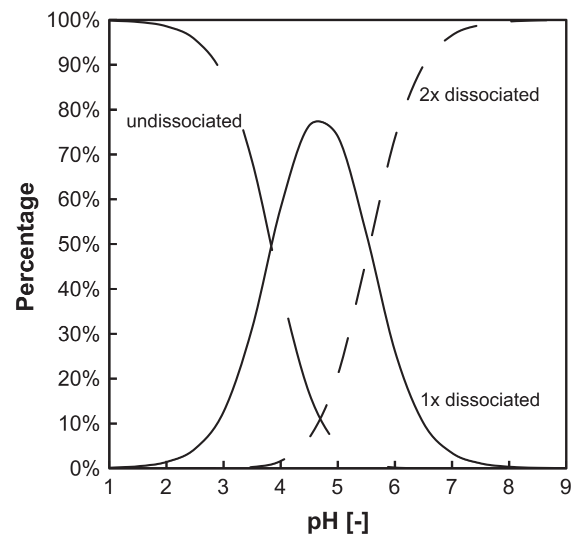

Fig. 4. Repartition of the itaconic acid species depending on the pH.

by [7,9]. The transport behavior of itaconic acid during electrodialysis without bipolar membranes, including both itaconic acid and disodium itaconate, has been analyzed and modeled using the extended Nernst–Planck equation [12]. However, continuous production of itaconic acid by means of electrodialysis using bipolar membranes and its integration into fermentation processes have been barely investigated at relevant process conditions. In fact, by employing bipolar membranes, the stack needs to be operated at current densities above the limiting current density [13] of the monopolar membranes. For simple salt solutions mass transport occurs even though the diffusional boundary layer is fully polarized. This is attributed to electroconvection [14]. Transport studies above the limiting current density for weak electrolytes or organic acids barely exist.

2. Background

2.1. Dissociation behavior of itaconic acid

Itaconic acid is an organic acid dissociating twice – its pK_a values lie at pH 5.45 and 3.84. Due to the dissociation behaviour of itaconic acid the electrodialysis process can turn out rather complex. Besides, the solution is non-ideal and the electrolyte equilibrium of itaconic acid solutions depends on pH value and ionic strength. The overall transport resistance depends on ionic charge and activity distribution. Fig. 3 shows the ideal pH and conductivity as functions of itaconate and sodium concentrations. It is derived from the calculation of the dissociation equilibria of itaconic acid and measurements of its electrical conductivity. Above the first pK_a value of 5.45, itaconic acid is completely dissociated. Fig. 4 shows the ideal equilibrium state of the three species of itaconic acid depending on the pH of the solution.

At that point the solution is highly conductive. In regions of lower pH itaconic acid is not dissociated and therefore electrical conductivity is decreased. In order to adjust the pH value, sodium hydroxide can be added to the solution. In turn, the increased sodium concentration increases the electrical conductivity as more ions are available for transporting the current. This concentration dependence results in an important boundary condition: a low concentration of ion speciation increases the resistance of the membranes and should be avoided.

2.2. Transport limitations at ion exchange membranes

During electrodialysis, the electrical potential established by the electrodes causes transport of the ions through solution and membranes. Through Faraday's law on ionic mass transfer, the electric current density in the outer electrical circuit is related to