Experimental and mathematical study of multicomponent ion transport in a Nafion membrane at high current densities

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The productivity of an electrochemical cell is determined by the current density and the selectivity of the ion-selective membrane that separates the anode and cathode compartments. For industrial processes, the productivity is limited by mass transfer to the electrodes. At current densities that exceed the mass transfer rate limit, undesired reactions occur. The mass transfer rate at the electrodes can be augmented with spinning disc electrodes and by using highly concentrated systems. This way, much higher current densities can be attained. However, virtually no data exists on the performance of ion-selective membranes at high current densities. The selectivity and conductivity of the membrane at high current densities are vital to assess the performance of the electrochemical cell and the process economics. Therefore, this paper presents data for membrane performance at high current densities up to 16 $kA.m^{-2}$. Furthermore, the ion transport in the membrane is modeled with the Nernst-Planck equations and with the Maxwell-Stefan equations [1]. The Nernst-plank equation neglects the interactions of ions and according to literature it is valid for dilute concentrations [2]. The Maxwell-Stefan equation takes the interaction of different species into account. However, it requires reliable data for diffusion coefficients [3]. The non-ideal behavior of the highly concentrated sodium hydroxide solution is modeled with the Pitzer activity model. The boundary conditions are determined with the Donnan equilibrium [4,5].

The model is validated with experiments performed in a temperature controlled electrolysis cell, using a perfluorinated sulfonate membrane, Nafion 1110, to separating the anode and cathode compartments. Sodium hydroxide is used as an electrolyte solution in order to monitor the transport of sodium ions and back-migration of hydroxyl ions to the cathode and the anode compartments respectively. The potential drop over the membrane is measured using two Haber-Luggin capillaries with reference electrodes and the tips of the capillary tubes close to either side of the membrane [4]. The selectivity of the membrane to sodium ions and hydroxyl back-migration is studied by measuring the concentration change in anode and cathode compartments and the total current passed through the membrane in a certain amount of time. The potential drop over the membrane and the membrane selectivity are determined for current densities up to 16 $kA.m^{-2}$ for a sodium hydroxide system with concentrations of 10 wt% to 32 wt%.

The Nernst-Planck model predicts that an increase in current density from 2 $kA.m^{-2}$ to 10 $kA.m^{-2}$ increases the positive ion flux from 0.02 $mol.m^{-2}s^{-2}$ to 0.1 $mol.m^{-2}s^{-2}$. The experiments show a similar trend in increase of positive ion flux from 0.02 $mol.m^{-2}s^{-2}$ to 0.07 $mol.m^{-2}s^{-2}$, however, with a clear reduction in selectivity. The model predicts a significant drop in membrane resistance from 0.045 $ohm.cm^2$ to 0.04 $ohm.cm^2$. The experiments show a bigger drop in membrane resistance from 1.3 $ohm.cm^2$ to 0.53 $ohm.cm^2$. Possibly, the decrease in selectivity measured experimentally, results in a lower voltage drop over the membrane. The transport of hydroxyl ions is much easier through the membrane than the transport of sodium ions.

Keywords: multicomponent ion transport, Nernst-Planck Maxwell-Stefan, membrane resistivity, membrane selectivity, high current density

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