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Ion Exchange in Countercurrent Electrolysis in a Porous Membrane

Kyosti Kontturi[a]; Hannu Revitzer[a]
[a] LABORATORY OF PHYSICAL CHEMISTRY AND ELECTROCHEMISTRY HELSINKI, UNIVERSITY OF TECHNOLOGY KEMISTINTIE 1, ESPOO, FINLAND

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NOTE

Ion Exchange in Countercurrent Electrolysis in a Porous Membrane

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KYÖSTI KONTTURI and HANNU REVITZER

LABORATORY OF PHYSICAL CHEMISTRY AND ELECTROCHEMISTRY
HELSINKI UNIVERSITY OF TECHNOLOGY
KEMISTINTIE 1, SF-02150 ESPOO, FINLAND

In many separation processes for electrolytes the economy of the process could be improved if ion exchange could be carried out simultaneously with the separation without additional stages; i.e., when, for instance, separating potassium chloride from a mixture of sodium and potassium chlorides, the anion could be replaced by the hydroxyl ion, thus producing, instead of potassium chloride, more valuable potassium hydroxide. In fact, in the separation of cations an often desired ion-exchange reaction is the above-mentioned replacement of some anion by the hydroxyl ion.

Studies concerning the use of countercurrent electrolysis in a porous membrane as a separation method for ions (*1-7*) have led to a cell construction which efficiently utilizes the separation processes taking place both in the porous membrane and in the ion-exchange membrane (*8*, *9*). Because countercurrent electrolysis comprises electrochemical processes at the electrodes—to maintain the electric current necessary for the process—it is possible to a certain extent to choose electrode reactions so that they serve as a source of the desired ion, e.g., hydroxyl ions. To elucidate this idea, consider cell construction with two separation units for separating cations. The cell is schematically described in Fig. 1.

In principle, the ion exchange can be done by the following two procedures. The hydroxyl ion are produced at the cathode and trans-

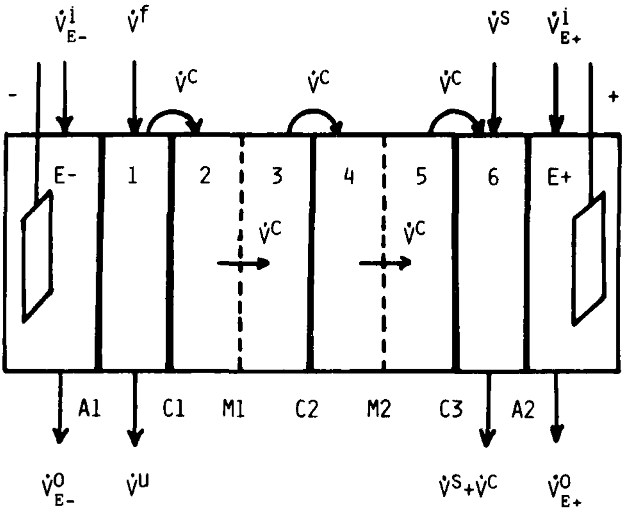

FIG. 1. Schematic drawing of the cell for cation separation with two separation units. A1 and A2 are the anion-exchange membranes; C1, C2, and C3 are the cation-exchange membranes; M1 and M2 are the porous membranes. The flow rates are as follows: $\dot{V}^f$ is the water feed, $\dot{V}^u$ is the outflow of enriched electrolyte solution, $\dot{V}^c$ is the convection, $\dot{V}^s$ is the feed of solution to be separated, and $\dot{V}^i_{E+,-}$ and $\dot{V}^o_{E+,-}$ are the circulating flows in the electrode compartments E+ and E−. For the operational details, see Refs. *8* and *9*.

ferred through the anion-exchange membrane (A1). When stationary state has been attained, the anions in the feed solution to Compartment 6 have been completely replaced by the hydroxyl ions in Compartments 1-5, and thus also in the product stream ($\dot{V}^u$). To maintain hydroxyl production, only water has to be added to the cathode compartment. This means that $\dot{V}^o_{E-} = 0$, but because of electroosmotic water flow through the ion-exchange membrane, the flow rates $\dot{V}^o_{E+}$ and $\dot{V}^i_{E-}$ have to be determined separately for each particular experimental case.

However, it is not always possible to achieve such an electrode reaction to produce the wanted anions (or cations in the case of separating anions). But we always have a chance to circulate a properly chosen mixture in the electrode compartment. For example, if the chloride ion is to be ion exchanged for the nitrate ion, a mixture of sodium nitrate with a calculated amount of nitric acid, enough to neutralize the hydroxyl ions formed, can be circulated in the cathode compartment.

We conducted two experiments in the cell presented in Fig. 1 and described in detail in Ref. 9. The systems studied were as follows: A mixture of $NaCl-KCl-H_2O$, the total concentration of which was 0.2 mol/dm^3 and a ratio of $c_{Na^+}/c_{K^+} = 1$, was fed into Compartment 6. In the first experiment hydroxyl ions were produced in cathode reaction (1):

$$H_2O + e^- \rightarrow \tfrac{1}{2}H_2 + OH^- \quad (1)$$

The electric current transfers hydroxyl ions through the anion-exchange membrane into the actual separation cell (Compartments 1–6). Because of cation-exchange membrane C3, the chloride ions are not able to enter into Compartments 1–5. In the second experiment the feed solution into Compartment 6 was the same as in the first experiment, but a mixture of sodium nitrate and nitric acid was circulated in the cathode compartment. The electrode reaction is, of course, identical to Eq. (1), but due to the nitric acid the hydroxyl ions formed are completely neutralized. As a result, only nitrate ions are transferred through the anion-exchange membrane A1. In the experiments the electric current, the convection, the rate of water feed into Compartment 1, and the rate of outflow from Compartment 1 were the same as in Ref. 9 for the case of two porous membranes. Thus the total concentration in the outflow stream from Compartment 1 was 0.01 mol/dm^3, and the selectivity ratio in both measurements was $S = 19$ when the current efficiency with respect to the ions to be separated was $\eta_{\text{I}}^{\text{c}} = 0.161$. The model presented in Ref. 8 predicts this behavior quite well.

In the first experiment the product stream contained only KOH and NaOH, and in the second experiment it contained KNO_3 and $NaNO_3$. The product streams did not contain detectable amounts of chloride ions. Account must be taken of the fact that in the case of concentrated solutions in the cell—which means much higher electric current densities—it is possible that co-ion leak can transfer trace amounts of chloride ions to the product stream. The magnitude of this effect can be estimated by using data on the free salt content in the ion-exchange membranes. Furthermore, an increase in the number of separation units decreases the possibility of the influence of co-ion leak.

Studies of countercurrent electrolysis in a porous membrane have shown that it is a potential way to separate electrolytes. Since we can also include the possibility of carrying out the ion exchange of common ion or ions while processing the actual separation, the potential is further increased.

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