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STUDY OF CATION EXCHANGE MEMBRANES MODIFIED FOR THEIR APPLICATION IN THE LIOH PRODUCTION BY MEMBRANE ELECTROLYSIS

The production of lithium compounds worldwide has increased due to its use in the manufacture of lithium batteries. Among the compounds destined for this market are lithium carbonate and lithium hydroxide, where each one has a specific demand depending on the material to be manufactured [1]. For high-capacity lithium-ion batteries such as NMC, lithium hydroxide as a precursor provides the cathode material with better electrochemical properties compared to lithium carbonate [2].

The conventional lithium hydroxide production process is long and involves the production of lithium carbonate, which in turn is transformed into lithium hydroxide with low conversion efficiencies. To overcome this problem, the application of membrane electrolysis was proposed, which allows LiOH to be produced directly from LiCl from concentrated brines. In the use of membrane electrolysis, an electrochemical reactor with two compartments is used, which are separated by a cation exchange membrane that allows the flow of positively charged ions through it. A LiOH solution is used as catholyte and a concentrated LiCl solution is used as anolyte. However, currently this process has a low LiOH production efficiency, and on the other hand, the presence of impurities in the natural brine such as Na^{+}, K^{+}, Ca^{2+} and Mg^{2+}, cause a reduction in efficiency and a reduction in purity of the final product because they will migrate through the cation exchange membrane [3].

The first part of the problem was solved (work in patenting stage) through an exhaustive study of the electrode kinetics and the optimization of operational parameters, which allowed reaching a production efficiency of 90% and a specific energy consumption of 4.08 [kWh/kgLiOH] compared to 75 % of efficiency currently reported by patents.

This report deals with the second part of the problem, whose solution consists in the surface modification of the Nafion 177 cation exchange membrane by polyelectrolyte deposition. Through the use of polydopamine (PDA) and polyethyleneimine (PEI), it is possible to provide the surface of the membrane with a positively charged layer, so that in this way, due to electrostatic effects, it is capable of repelling divalent ions such as Ca^{2+} and Mg^{2+}, allowing preferential migration of monovalent cations.

Two types of surface modifications were made, the first (Mod-1) with a mixture of PDA/PEI and the second (Mod-2) with a mixture of PDA/PEI and aluminum nanoparticles. Both modifications were studied at three different concentrations of modifiers, and they were characterized.

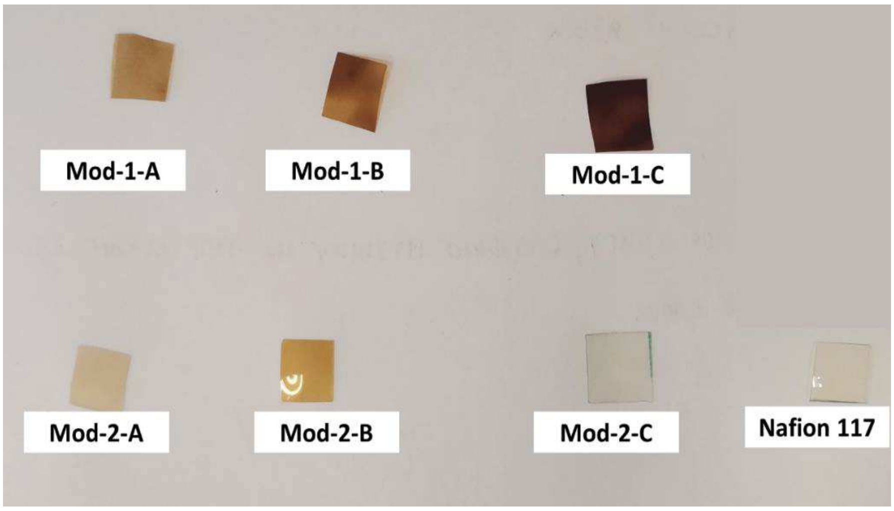

Figure 1. Modified membranes Mod-1(A,B,C), Mod-2 (A,B,C) and non-modified membrane Nafion 117

Figure 1 shows two types of modification compared to Nafion 117, where the effect of the concentration of the modifiers can be observed, where "A" is the lowest concentration and "C" is the highest concentration. The effect of polymerization time for dopamine can also be observed, since Mod-1 had 4 hours of polymerization and Mod-2 had 2 hours of polymerization.

a

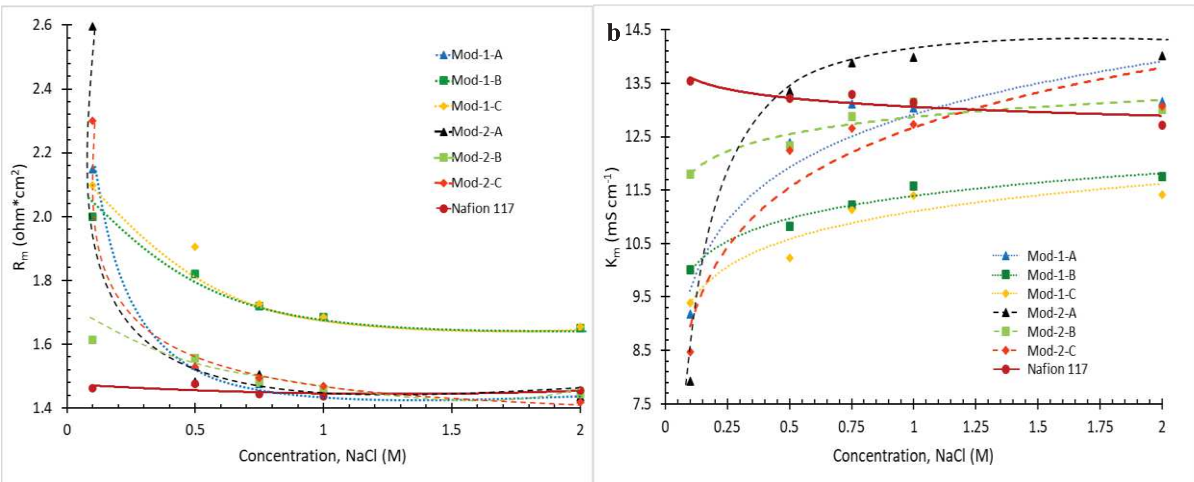

Figure 2. a) Electrical resistance, b) Electro-conductivity for Mod-1(A,B,C), Mod-2 (A,B,C) and unmodified membrane Nafion 117

Regarding the study of the physical properties of the membranes, the values of electrical resistance and conductivity were determined using the "Differencial Method". As can be seen in figure 2 a), the electrical resistance of the Mod-1 membranes increased, while the Mod-2 membranes reach electrical resistance values similar to those of the pristine Nafion 117 membrane at concentrations greater than 0.5M. In the same way, the electrical conductivity presents a trend according to the values of electrical resistance, however, it should be noted that there is a significant variation in its values at the same concentration as observed in figure 2 b). This effect is attributed to the difference in the thickness of the membrane, since the different modifications endowed the membranes with greater water absorption[4, 5].

As figure 3 a), the diffusion permeability of Nafion 117 increases after its modification. This parameter directly affects the value of the Na^+ transport number (figure 3 b)): the Nafion 117 membrane has the highest transport number and the values for the modified membranes are less. That is, the modified membranes will allow a greater flow of co-ions through them. However, this difference is not very significant, in percentage the Na^+ transport number was reduced between 0.7 and 1%.

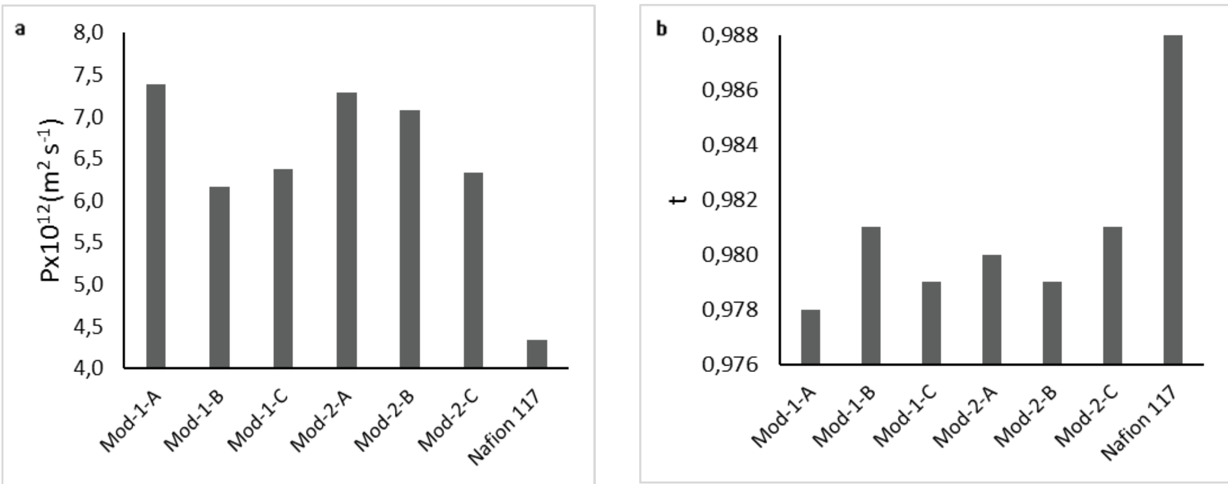

Figure 3. a) Diffusion permeability, b) Transport number for Mod-1(A,B,C), Mod-2 (A,B,C) and non-modified membrane Nafion 117 in a 2M NaCl solution

Analyzing the properties of the studied membranes, it was determined that the ones that achieved the best behavior are the Mod-1-B and Mod-2-C membranes, which will later be tested with LiCl brines and different impurities, to analyze the separation capacities. between divalent and monovalent ions, emphasizing lithium transport. Below are the SEM images of the Mod-1-B and Mod-2-C membranes compared to the Nafion 117, where we can see the deposition of PDA/PEI over surface of modified membrane (figure 4).

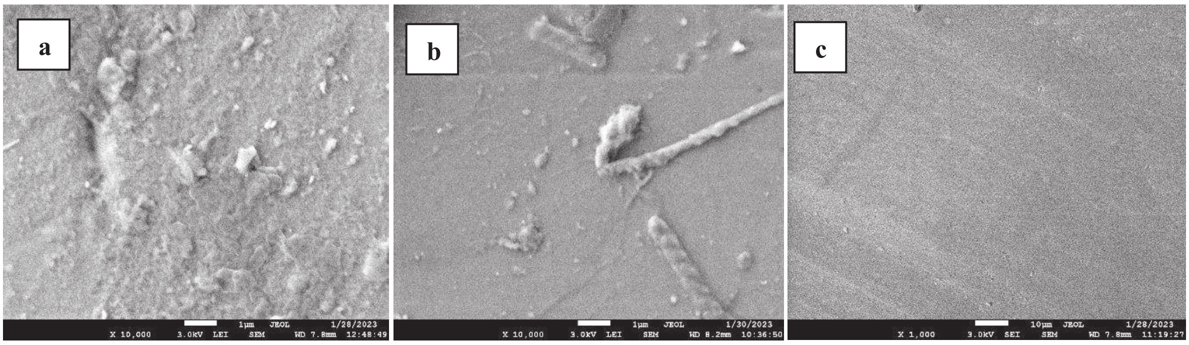

Figure 4. SEM images of a) Mod-1-B, b) Mod-2-C, c) Nafion 117

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