Synthesis of Doctoral Dissertation
Doctoral Program in Materials Science and Technology (36th Cycle)

New technologies and materials for energy harvesting from water

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Graphene oxide (GO) membranes have been proven to be ion selective thanks to their oxidized functional groups which are naturally present on their surface. This ion selectivity, together with a good mechanical strength, low cost, and simple synthesis make GO a great alternative material to conventional costly polymers to produce ion exchange membranes. This work focuses on how to produce GO membranes as ion exchange membranes with a scalable approach and tunable performances.

Their physicochemical properties were subsequently investigated by means of selected characterization techniques. Results showed that GO membranes present good ion selectivity and size exclusion towards monovalent cations reaching a permselectivity of up to 97%. The addition of binders was also investigated to improve the membranes' mechanical properties. Interestingly, UV light irradiation of GO membranes was also proposed as a green reduction method. GO reduction increases the permselectivity due to both a decrease in the dimension of the nanochannels and a reduction in the swelling degree of the membranes. Finally, the ionic resistance of the membranes was measured by impedance spectroscopy,

achieving 4.6 Ω cm^2, orders of magnitude lower than the state-of-the-art graphene oxide-based membranes, leading to a maximum power density of 0.72 W m^{-2}.

However, graphene oxide membranes still presented higher ionic resistances than commercial membranes. To address this issue, $Al(OH)_4^-$ anions were incorporated into graphene oxide membranes to increase their spontaneous negative surface charge. The anions were successfully formed and encapsulated through a reaction with the alumina support under alkaline conditions during the membrane formation. The membranes' physicochemical properties were analyzed using selected characterization techniques. The incorporation of $Al(OH)_4^-$ anions significantly reduced the ionic resistance to 2 Ω cm^2, increasing the power density to 1.53 W m^{-2}. A model of the system confirmed the anchoring of these ions within the membrane matrix and their role in boosting the charge of the membrane and, therefore, their electrochemical properties. The study delved into the utilization of GO membranes as monovalent-selective membranes, an approach to boost reverse electrodialysis power densities. The membranes demonstrated impressive selectivity, overcoming 70 folds for divalent cations over K^+.

As an ultimate step to increase the Technology Readiness Level of the production of graphene oxide membranes, Roll-to-Roll technique was introduced for a continuous scalable process. Aluminum foil was selected as an alternative support to glass and a novel detachment process was proposed: aluminum etching in KOH solution. This process resulted in highly reduced scalable GO membranes, leading to superior permselectivity but too high ionic resistance. These results demonstrate the feasibility of this approach even if further studies must be pursued to fine-tune the membrane performance.