

New membranes for CO₂ electrochemical reduction

Teixeira, F. C.^{1*}, Teixeira, A. P. S.², Messias, S.³, Martins, R.³, Mendes, J. M.³, Reis

Machado, A. S.^{3,4}, Rangel, C. M.^{1*}

¹ Laboratório Nacional de Energia e Geologia, I.P., 1649-038 Lisboa, Portugal

² Departamento de Ciências Médicas e da Saúde, ESDH & LAQV- REQUIMTE, IIFA, Universidade de Évora, 7000-671 Évora, Portugal

³ i3N/CENIMAT, Department of Materials Science, NOVA School of Science and Technology and CEMOP/UNINOVA, Campus de Caparica, 2829-516 Caparica, Portugal

⁴ LAQV, REQUIMTE, Chemistry Department, NOVA School of Science and Technology, Campus de Caparica, 2829-516 Caparica, Portugal

*Email: fatima.teixeira@lneg.pt; carmen.rangel@lneg.pt

The use of CO₂ as a valuable feedstock to obtain new useful fuels and materials, such as CO, alcohols, formic acid and hydrocarbons, has become an important research field that can contribute to valuable strategies in carbon resource utilization, such as the Electrochemical CO₂ Reduction (ECR). The process is carried out in electrolyzers, which have a membrane as a key component to separate the two-half cells, with performance and sustainability strongly linked to membrane properties, including ionic conductivity, chemical and structural stability and permeability of products and incoming and generated gases [1].

The aim of this work is the preparation and evaluation of a series of doped cation conductive membranes for use in low temperature CO₂ electrolysis, for increasing efficiency and minimizing gas crossover. The new membranes were prepared by the incorporation of bisphosphonic acids dopants into the matrix of selected polymers: widely used Nafion, and a lower cost, non-fluorinated alternative, SPEEK. The choice of dopants is justified since their incorporation improved ion conducting properties of the membranes as well as their durability, as indicated in previous studies by the authors [2,3].

New membranes, with a 7x7 cm dimension, were tested in an optimized, two compartment, purposely build reactor for CO₂ reduction [4], employed to obtain syngas, operating at 45 °C, pressurized at 10 bar, using 10% EMIMOTf ionic liquid as electrolyte and 1437 °C of charge. Membrane performance was compared with a PSFA-based Nafion-like commercial membrane, 10120-PK from Fumatech, used as standard and tested in the same experimental conditions. Electrolyses results using the new membranes are compared in terms of productivities of CO₂ reduced products, faradaic efficiencies, energy efficiencies and crossovers. These results showed that these membranes are a promising material for ECR.

Keywords: carbon dioxide; electrolysis; cation exchange membrane; bisphosphonic acids

Acknowledgements: This work was financed by national funds from FCT – Fundação para a Ciência e a Tecnologia, I.P., through projects PTDC/EQU-EPQ/2195/2021-CO2RED and LAQV-REQUIMTE projects UIDB/50006/2020, UIDP/50006/2020 and LA/P/0008/2020, as well as Associate Laboratory Institute of Nanostructures, Nanomodelling and Nanofabrication—i3N projects UIDP/50025/2020, UIDB/50025/2020 and LA/P/0037/2020. S. Messias acknowledges FCT for doctoral fellowship SFRH/BD/147219/2019. Project M-ECO2- Industrial cluster for advanced biofuel production, C644930471-00000041, co-financed by PRR (Next Generation EU) is also acknowledged.

[1] Varhade, S.; Guruji, A.; Singh, C.; Cicero, G.; García-Melchor, M.; Helsen, J.; Pant, D.; *ChemElectroChem* 12 (2025) e202400512.

[2] Teixeira, F. C.; de Sa, A. I.; Teixeira, A. P. S.; Ortiz-Martinez, V. M.; Ortiz, A., Ortiz, I.; Rangel, C. M.; *Int. J. Hydrogen Energy* 46 (2021) 17562-17571.

[3] Teixeira, F.C.; de Sá, A. I.; Teixeira, A. P. S.; Rangel, C.M.; *Int. J. Hydrogen Energy* 8 (2023) 37489-37499.

[4] Messias S., Sousa M. M., Nunes da Ponte M., Rangel, C. M., Pardal T., Reis Machado A. S., *React. Chem. Eng.* 4 (2019) 1982-1990.