

Nanoporous anodic alumina membranes as gas diffusion layers for CO₂ reduction catalysts

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The negative impact of global warming caused by the anthropogenic release of CO₂ into the atmosphere has prompted governmental institutions to take drastic actions to mitigate its outcome. Therefore, converting CO₂ into renewable fuels,^[1,2] imposes itself as a straightforward alternative since it generates added revenues.

The electrochemical reduction of CO₂ constitutes one such approach. Despite being promising for the transformation of CO₂ into products such as methane, ethylene or ethane, it is not yet competitive on the industrial scale. Although the design of industry-compatible electrolyzers is rather well established, their typically poor selectivity and short lifetime are still major limiting factors. So-called flow cells and membrane electrode assembly (MEA) electrolyzers are the most viable alternatives for industrialisation;^[3–5] however, their most important component, namely the **gas diffusion layer (GDL)**, is not yet reliable beyond laboratory-scale systems. As such, it is generally accepted that the development of reliable gas diffusion layer/catalysts assemblies allowing CO₂ electroreduction rates of over 200 mA/cm² with lifetimes exceeding 1000 hours will be the key parameters for allowing the technology to reach the industry.^[6,7]

Considering the above prerequisites, we found that nanoporous anodic alumina (NAA) provides a convenient method to manufacture GDLs according to the specific requirements of a given catalyst deposited on its top surface. The versatility of the NAA-GDL fabrication process offers an extremely powerful tool for depositing metals with any given combination of thickness, aperture diameter, and hydrophobicity. In this respect, NAA-GDLs bridge the existing knowledge gap in the design and manufacture of durable GDLs

The manufacture of the GDLs was carried out using a well-established anodization procedure originally developed by Matsuda and co-workers. Most importantly, the produced NAA layers benefit from the fact that their so-called residual barrier layer can be selectively dissolved using procedures previously described Marsal and co-workers.^[8,9] This provides NAA laminas with pores fully opened at both ends (Figure 1a) upon selectively dissolving the remaining aluminium backside of the substrate (Figure 1b). The membrane was shown to have far greater mechanical strength than typical carbon-based state-of-the-art GDLs when the thickness of the NAA exceeded 50 μ m (figure 1c), withstanding shear and compression stresses. Upon further deposition of a metal catalyst *via* sputter coating a GDE is formed.

The catalytic properties of the GDEs fabricated from the above GDLs were assessed in a dedicated flow cell system specifically designed to accommodate round-shaped 20 mm diameter NAA-GDE substrates with a 1 cm² active area. Preliminary results indicate that the current design is a nearly perfect fit with the requisites of the NAA layers (Figure 2). Early trials showed that CO₂ gas diffuses through the NAA-GDL to the silver catalyst and reduces to CO with a **faradic efficiency of over 60% under a 50 mA/cm²** electrolysis current (Figure 2d).

References

- [1] M. M. Halmann, *Chemical fixation of carbon dioxide: methods for recycling CO₂ into useful products*, CRC Press, Boca Raton, **1993**.
- [2] M. Aresta, Ed., *Carbon Dioxide Recovery and Utilization*, Springer Netherlands, Dordrecht, **2003**.
- [3] B. Endrődi, G. Bencsik, F. Darvas, R. Jones, K. Rajeshwar, C. Janáky, *Progress in Energy and Combustion Science* **2017**, 62, 133.
- [4] C. Xia, P. Zhu, Q. Jiang, Y. Pan, W. Liang, E. Stavitski, H. N. Alshareef, H. Wang, *Nat Energy* **2019**, 4, 776.
- [5] D. Gao, P. Wei, H. Li, L. Lin, G. Wang, X. Bao, *Acta Physico Chimica Sinica* **2020**, 37, 2009021.
- [6] P. De Luna, C. Hahn, D. Higgins, S. A. Jaffer, T. F. Jaramillo, E. H. Sargent, *Science* **2019**, 364, eaav3506.
- [7] T. Burdyny, W. A. Smith, *Energy Environ. Sci.* **2019**, 12, 1442.
- [8] A. Santos, L. Vojkuvka, J. Pallarés, J. Ferré-Borrull, L. F. Marsal, *Journal of Electroanalytical Chemistry* **2009**, 632, 139.
- [9] M. P. Montero-Rama, A. Viterisi, C. Eckstein, J. Ferré-Borrull, L. F. Marsal, *Surface and Coatings Technology* **2019**, 380, 125039.

Figures

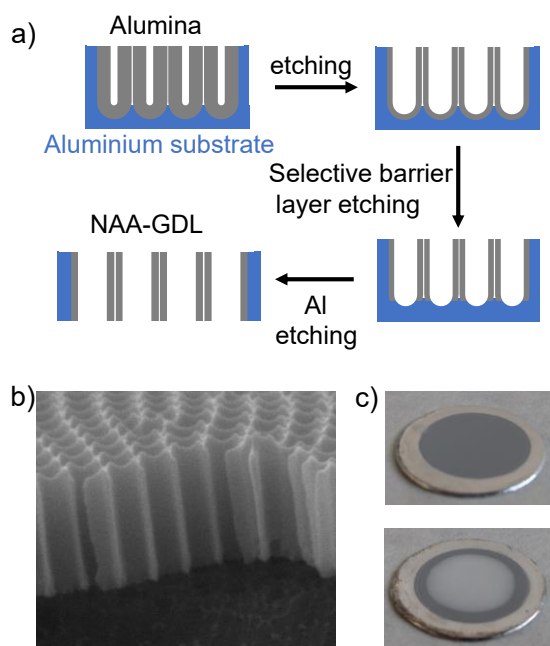


Figure 1. a) Schematic representation of the GDL fabrication procedure; b) SEM image of a very thin NAA lamina opened at both ends (disassembled from the aluminium substrate by mechanical means) obtained using such procedure (own work).; c) pictures of raw NAA substrates (top) and 90 μm -thick NAA-GDL, without aluminium backing (bottom)

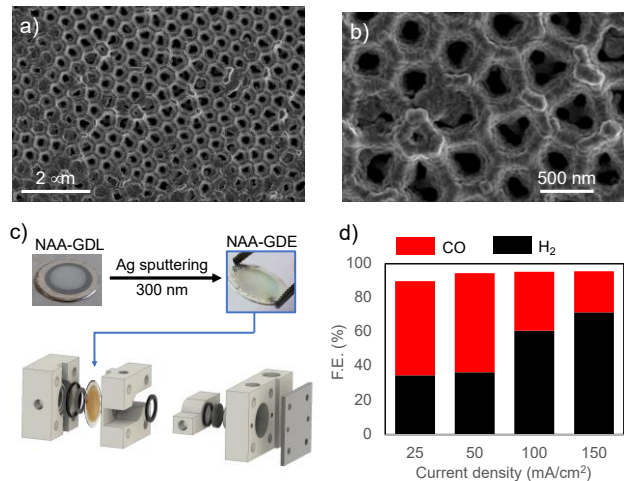


Figure 2. a) and b) Top SEM images of a very thin NAA lamina coated with a 300 nm (average) silver layer deposited via sputter coating showing the extent of the aperture (own work). The pores are not sealed despite the thick Ag layer; c) Pictures of an hydrophobysed GDL prior to the Ag deposition and picture of the final GDE. Drawing of the 3D printed home-built flow cell used in preliminary experiments, showing the catholyte compartment in which the NAA-GDE is held. d) Histogram of the faradic efficiency of the silver-coated NAA GDE from electrolysis experiments carried out at constant current.