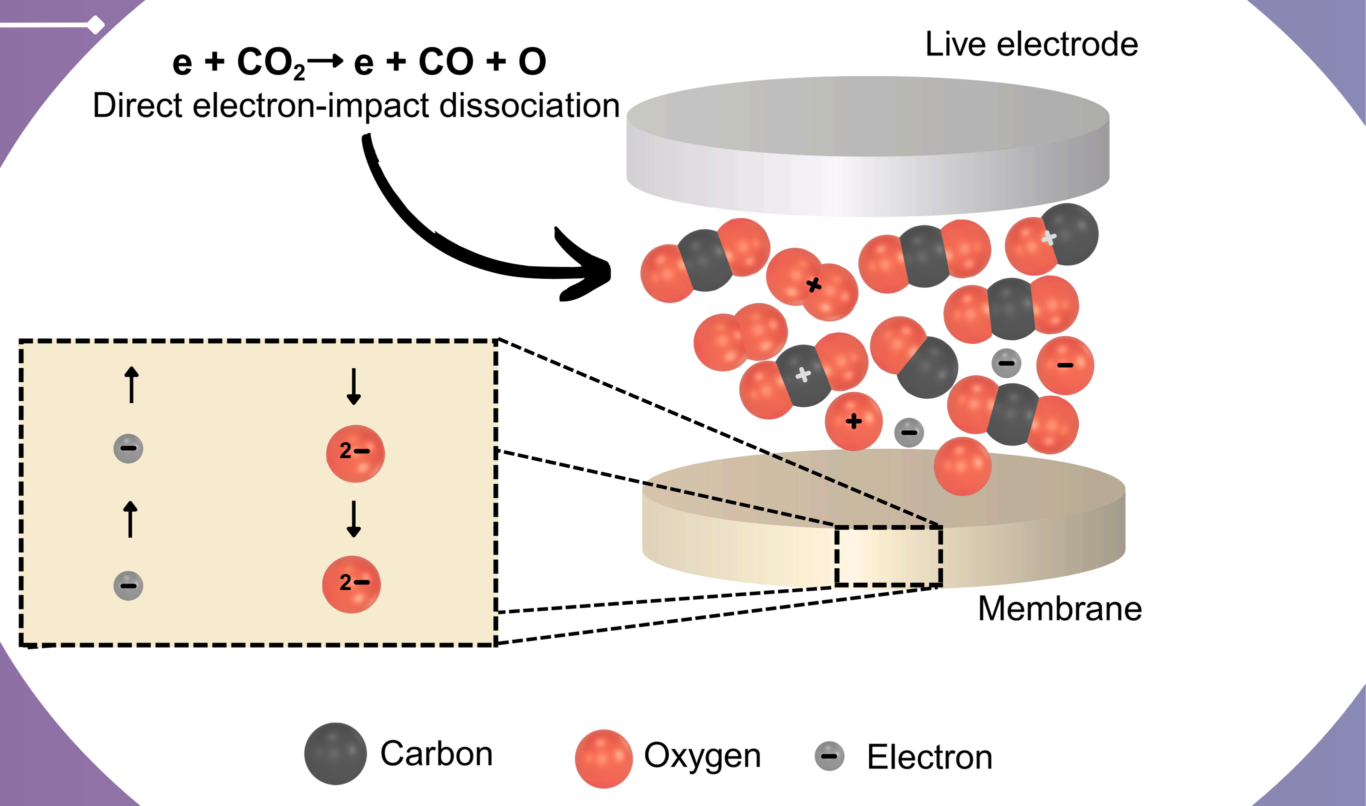
Multidimensional fluid modelling of reactor coupling plasma and oxygen separation membrane

Joana Araújo, 99496 (joanaaraujo@tecnico.ulisboa.pt)
Master's Thesis
Supervisors: Prof. Pedro Viegas[1] , Dr. Nuno Pinhão[1]
[1]Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Portugal

1. Introduction

Plasma-assisted CO_2 conversion in membrane reactors provides an alternative to thermochemical CO_2 conversion, eliminating the need for catalysts on the membrane surface and thereby avoiding issues such as catalyst deactivation [1]. This approach is attractive for O_2 production for industrial use and as an enabling technology for the colonisation of Mars. In this work, the operation of a Dielectric Barrier Discharge (DBD) reactor coupled with a Mixed Electronic Ionic Conductor (MIEC) ceramic membrane, for oxygen separation, is studied, with the goal of optimising an experimental reactor for CO_2 conversion and oxygen extraction.



2. Methodology

2D axisymmetric simulations in Elmer FEM
- Heat equation and Navier-Stokes equations → Temperature and velocity
- Electrostatic equation
- Open-source finite element software for multiphysical problems
- Mainly developed by the CSC - IT Center for Science

Models developed in Python
- Plasma global (0D) model
- 1D axial model (discharge gap + oxygen permeable membrane)

Electrostatic equation
$$\nabla \cdot \varepsilon \mathbf{E} = \rho$$

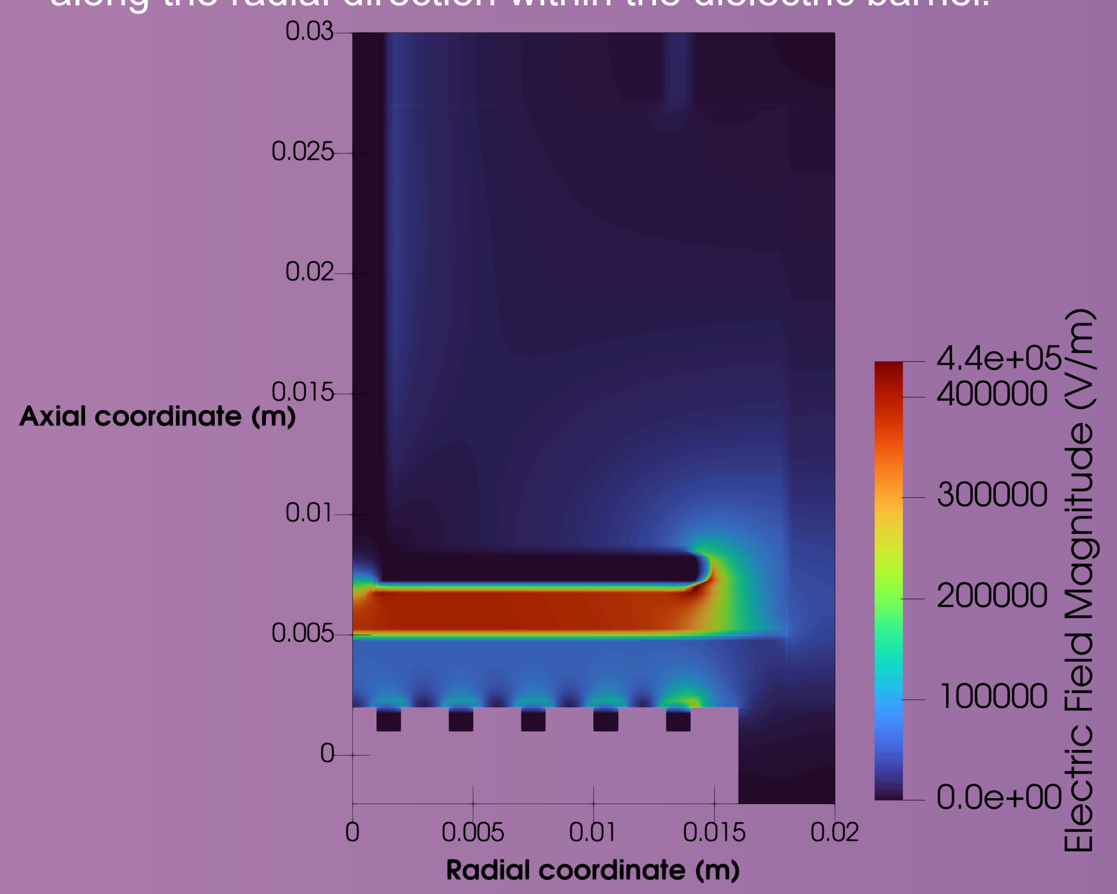
Species continuity equation
$$\frac{\partial n_i}{\partial t} + \frac{\partial \Gamma_i}{\partial x} + \frac{n_i}{t_r} + L_i = S_i$$

3. Results

3.1. Outcomes of the simulations in Elmer FEM

3.1.1. Electric field

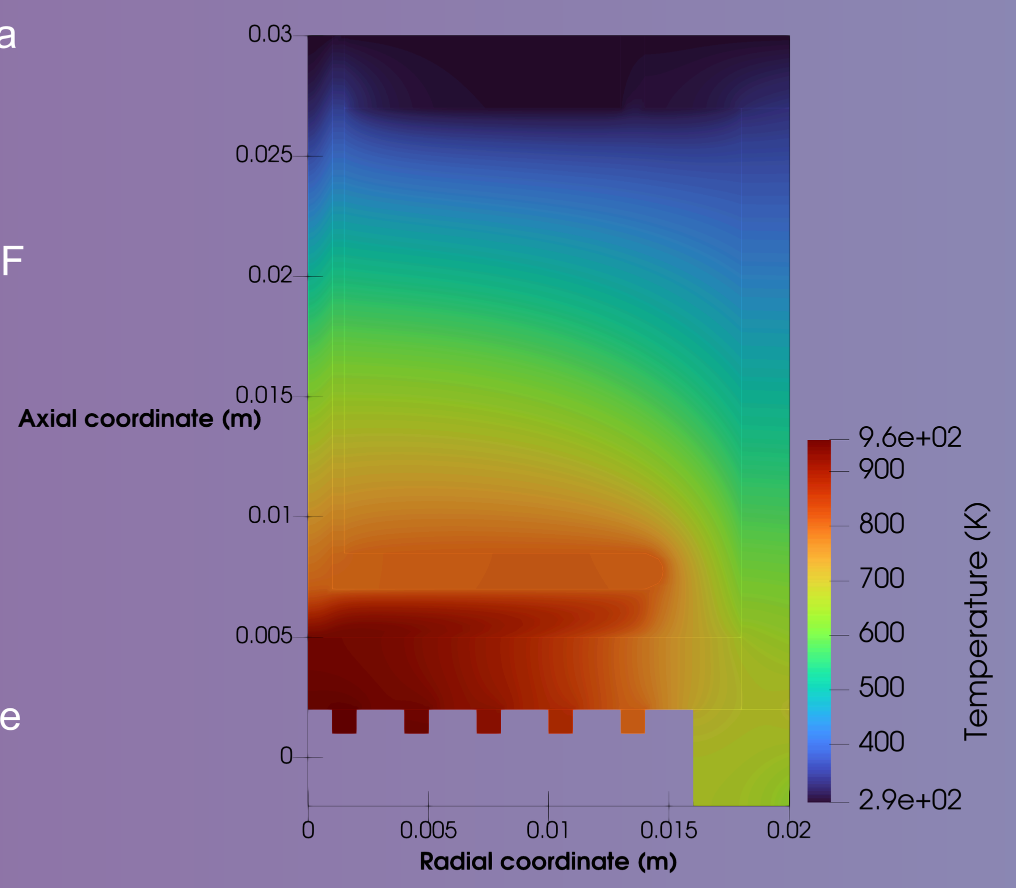
- The distribution of the grounded elements gives rise to meaningful oscillations in the electric field magnitude along the radial direction within the dielectric barrier.



Electric field distribution at the maximum voltage (1000 V).

3.1.2. Temperature and fluid velocity

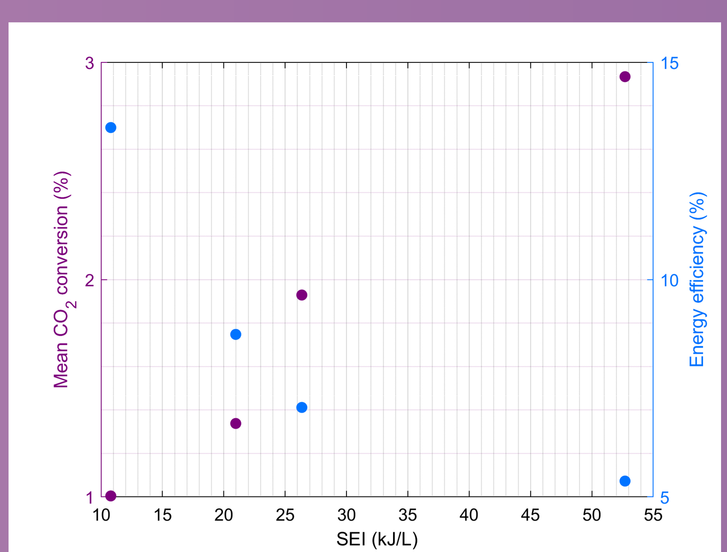
- Plasma processes induce an increase in the gas temperature within the discharge zone, as well in the temperature of the adjacent bodies. Evidently, this increase is more significant for a higher discharge power.
- Due to the low thermal conductivity of the membrane, a decrease in temperature with increasing radius is observed within the membrane. The non-stoichiometric oxygen of a BSCF membrane and the diffusion coefficient of oxygen anions increase with temperature [2]. Implicitly, due to this radial temperature gradient, at more outward positions, a lower number of oxygen vacancies will be observed and the oxygen diffusion through the membrane will be slower.
- The fluid velocity is determined by the combined effect of the forced convection associated with the gas flow imposed at the entry and the natural convection caused by the gas temperature variations and the resulting gas density gradients within the reactor.



Temperature distribution obtained at a flow rate of 10 ml/min, a discharge power of 12 W and a heating power of 10 W.

3.2. Results of the global (0D) model in Python

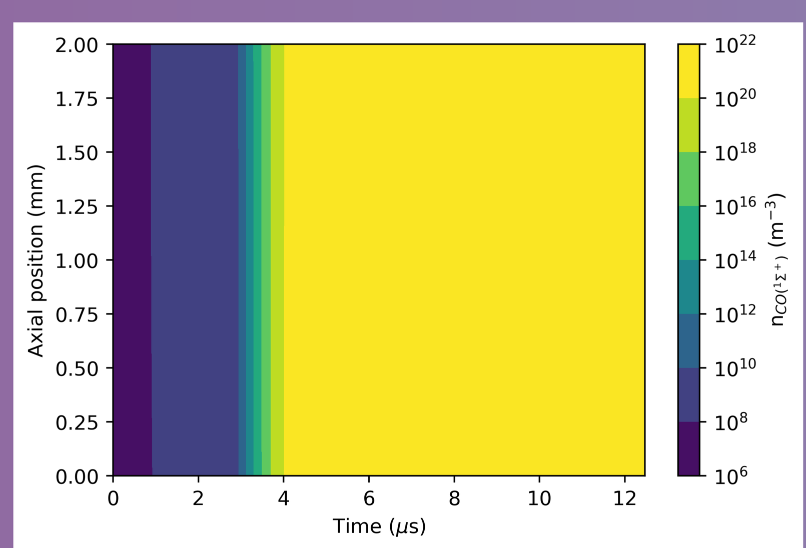
- A preliminary portrait of the CO_2 conversion and energy efficiency, which clearly illustrates the trade-off between them, is obtained at a very low computational expense.
- These results were determined using average power inputs, P, of 10 and 30 W, and the residence times, t_r, estimated from the results of the 2D simulations for flow rates of 10 and 20 mL/min. The Specific Energy Input (SEI) was calculated as $SEI = Pt_r/V_{plasma}$, where V_{plasma} is the plasma volume (1.2252 cm^3).



Mean CO_2 conversion and energy efficiency as a function of the SEI.

3.3. Results of the 1D axial model in Python

- The charge build-up on the upper surface of the dielectric changes the electric field distribution. Due to the higher electron mobility (compared to that of ions), and since a single-dielectric DBD setup is used, this charge accumulation is faster and more significant during the negative half-cycles. Hence, the gap voltage tends to be lower during the negative half-cycles. Consequently, the maximum electron number density is higher in positive half-cycles, leading to a greater CO_2 conversion during these half-cycles.
- Due to the relatively high frequency of the applied voltage, the timescale of electron-ion recombination is much longer than the time interval between successive discharge events [3]. This prevents full recombination of charge carriers between these events, further contributing for the differences between the positive and negative half-cycles.



Temporal evolution of the axial distribution of the CO number density. The ceramic upper surface is on bottom, and the lower surface of the electrode is on top.

4. Conclusions and Future Work

- It is necessary to carefully adjust the discharge and heating powers to ensure that the membrane remains at an optimal temperature for oxygen permeation (generally, > 700 ºC) without reaching its melting point (which is approximately 1250 ºC, according to experiments). Besides this, reactive species in the plasma can cause significant damage to the membrane, leading to performance deterioration [1].
- This 1D model is only suitable for a DBD operating in the homogeneous (glow) mode, as modelling a DBD in the filamentary (streamer) mode requires a 2D (or 3D) model [3,4]. In the future, advanced computational resources and techniques could be leveraged in order to build a feasible 2D model, which would provide a more complete portrait of the DBD operation and oxygen permeable membrane dynamics.

References

[1] Z. Liu, W. Zhou, Y. Xie, F. Liu, Z. Fang, G. Zhang, and W. Jin. Highly effective CO_2 splitting in a plasma-assisted membrane reactor. Journal of Membrane Science, 685:121981, 2023. doi:10.1016/j.memsci.2023.121981.
[2] E. Bucher, A. Egger, P. Ried, W. Sitte, and P. Holtappels. Oxygen nonstoichiometry and exchange kinetics of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$. Solid State Ionics, 179(21):1032–1035, 2008. doi:10.1016/j.ssi.2008.01.089.
[3] S. Ponduri, M. M. Becker, S. Welzel, M. C. M. van de Sanden, D. Loffhagen, and R. Engeln. Fluid modelling of CO_2 dissociation in a dielectric barrier discharge. Journal of Applied Physics, 119(9): 093301, 2016. doi:10.1063/1.4941530.
[4] K. Kourtzanidis. Full cycle, self-consistent, two-dimensional analysis of a packed bed DBD reactor for plasma-assisted CO_2 splitting: spatiotemporal inhomogeneous, glow to streamer to surface discharge transitions. Plasma Sources Science and Technology, 32(10):105016, 2023. doi:10.1088/1361-6595/ad0430.