Modelling the interaction between glow discharge plasmas and separation membranes for CO2 conversion

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Introduction

- Rising atmospheric CO_2 levels require efficient conversion technologies. Low-Temperature Plasmas (LTPs) provide an energy-efficient solution by utilising non-equilibrium electrons to dissociate molecules without high thermal input. To enhance conversion, Mixed Ionic-Electronic Conductor (MIEC) membranes can be integrated into the reactor to continuously separate oxygen from the mixture;
- This work represents a first step towards describing plasma-membrane coupled systems, focusing on the **development and validation of a self-consistent plasma model for CO_2 conversion**;
- The main goal is to evaluate the numerical stability, accuracy, and computational cost of different modelling approaches like Drift-Diffusion (DD) and Full Fluid Moment (FFM) against simplified benchmarks and experimental data.

CO_2 Simulations

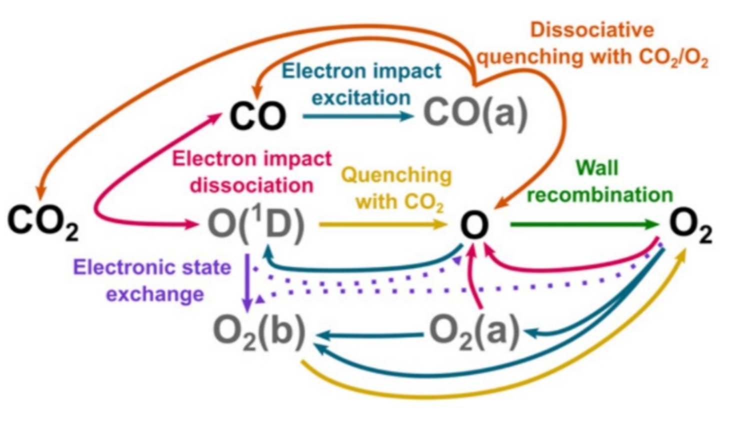
- DC working conditions:

$P = 0.5 - 1$ kPa, $T_g = 300$ K, $L = 4$ mm, $U = 400$ V, R = 1 cm

- Electrode BC: kinetic flux absorption for charged species and secondary electron emission, $\gamma_{SEE} = 0.01$;
- Chemistry reactions from [3], [4] and [5];
- Cylindrical wall reactions are considered as creation/loss terms with: [6], [7]

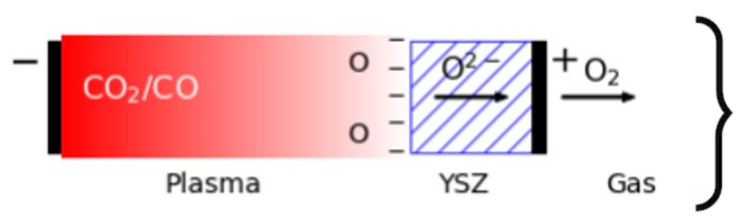
$$k_r = \frac{1}{\tau_{d,s}}, \quad \tau_{d,s} = \begin{cases} \dfrac{\Lambda^2}{D_n} + \dfrac{R(2-\gamma)}{\gamma\, v_{th}}, & s = \text{neutral} \\ \dfrac{\Lambda\, R}{2\, D_{\text{eff},s}} + \dfrac{2\, R}{v_{th}}, & s = \text{electron, ion} \end{cases}$$

$O_2(X)$	$O(^3P)$	$O_3(X)$	$CO_2(X)$	$CO(X)$	$C(X)$
$O_2(a^1\Delta_g)$	$O(^1D)$	O_3^*		$CO(a^3\Pi)$	
$O_2(b^1\Sigma_g^+)$					
O_2^+	O^+		CO_2^+	CO^+	
	O^-				



Species involved in the simulation and some of the key reactions considered. [3]

LoKI-1D Fluid Model & Numerical Implementation



Only the plasma component of the system has been implemented in the model so far.

1. Governing Fluid Equations

FFM Model

$$\frac{\partial n_s}{\partial t} + \frac{\partial (n_s u_s)}{\partial x} = S_s$$

$$\frac{\partial (n_s u_s)}{\partial t} + \frac{\partial}{\partial x}\left(n_s u_s^2 + \frac{p_s}{m_s}\right) = \frac{q_s}{m_s} n_s E + C_s$$

$$\frac{\partial (n_s \varepsilon_s)}{\partial t} + \frac{\partial}{\partial x}\left[(n_s \varepsilon_s + p_s)\, u_s\right] = q_s n_s u_s E + R_s$$

DD Approximation

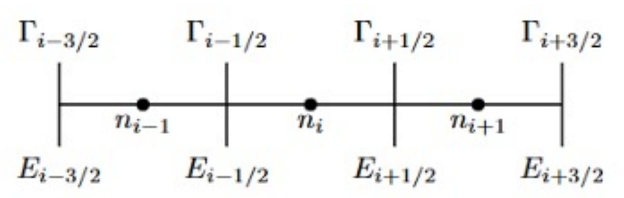
$$\frac{\partial n_s}{\partial t} + \frac{\partial}{\partial x}\left[\frac{q_s}{|q_s|} n_s \mu_s E - D_s \frac{\partial n_s}{\partial x}\right] = S_s$$

$$\frac{\partial (n_s \varepsilon_s)}{\partial t} + \frac{\partial}{\partial x}\left[\frac{q_s}{|q_s|} n_s \varepsilon_s \tilde{\mu}_s E - \tilde{D}_s \frac{\partial (n_s \varepsilon_s)}{\partial x}\right] = R_s$$

- Poisson's equation coupled to the transport equations: $\nabla \cdot \mathbf{E} = -\nabla^2 \phi = \frac{\rho}{\varepsilon_0} = \frac{e}{\varepsilon_0}(n_i - n_e)$

2. Spatial and Temporal Discretisation

- Spatial discretisation: Finite Volume Method (FVM);
- A discretisation of the system of equations leads to the expressions we must solve numerically for each cell i, at each CFL time step:

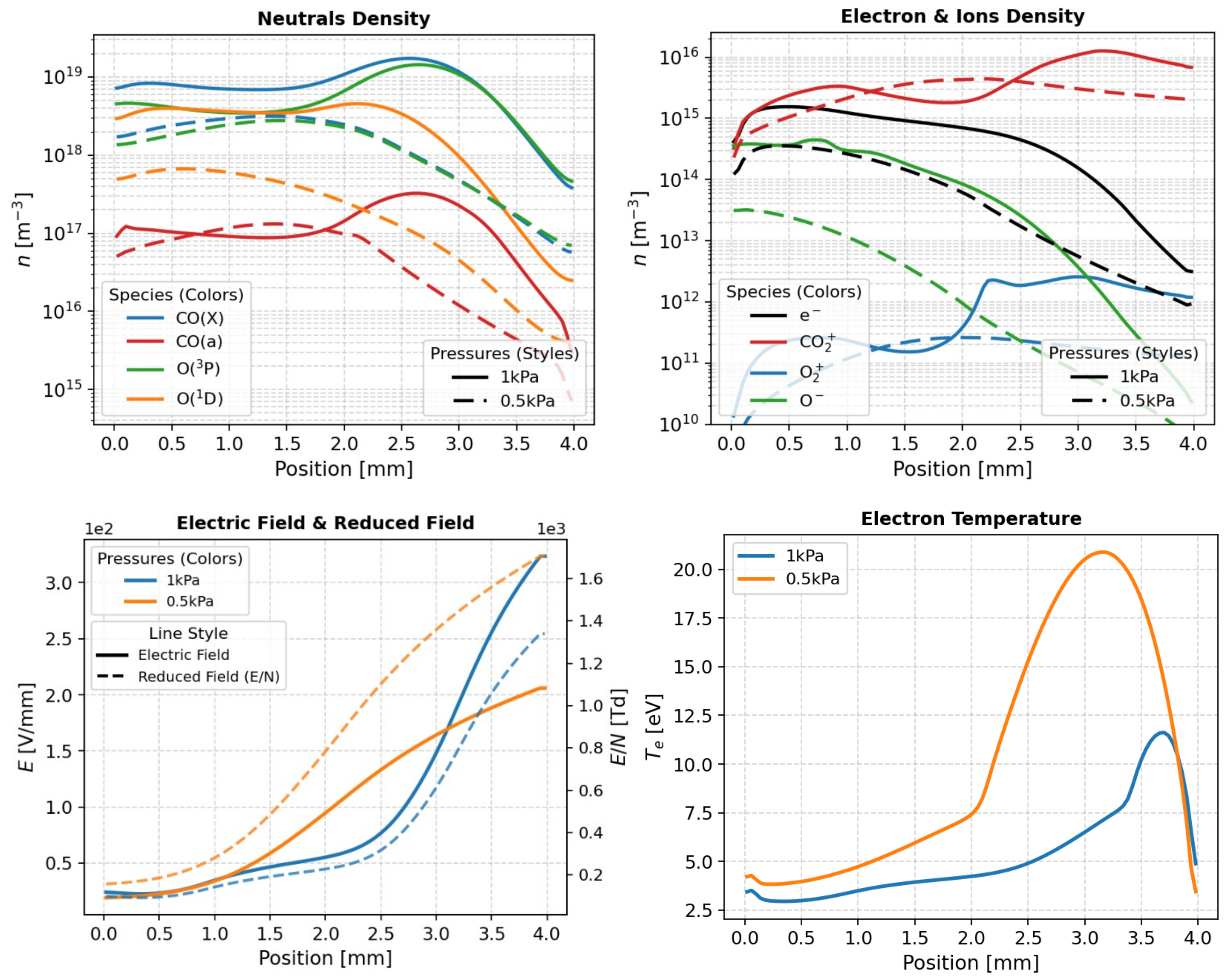


$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{U}_i = \mathbf{R}_i, \quad \mathbf{R}_i^t = -\frac{1}{\Delta x}\left(\mathbf{F}_{i+1/2} - \mathbf{F}_{i-1/2}\right) + \mathbf{S}_i$$

- Lax-Friedrich and Roe schemes implemented for FFM;
- Van Leer, superbee, Scharfetter-Gummel, etc. implemented for DD approximation;
- Explicit, Semi-Implicit and Implicit methods used to evolve the properties in time.

Early Results: Cathode Sheath

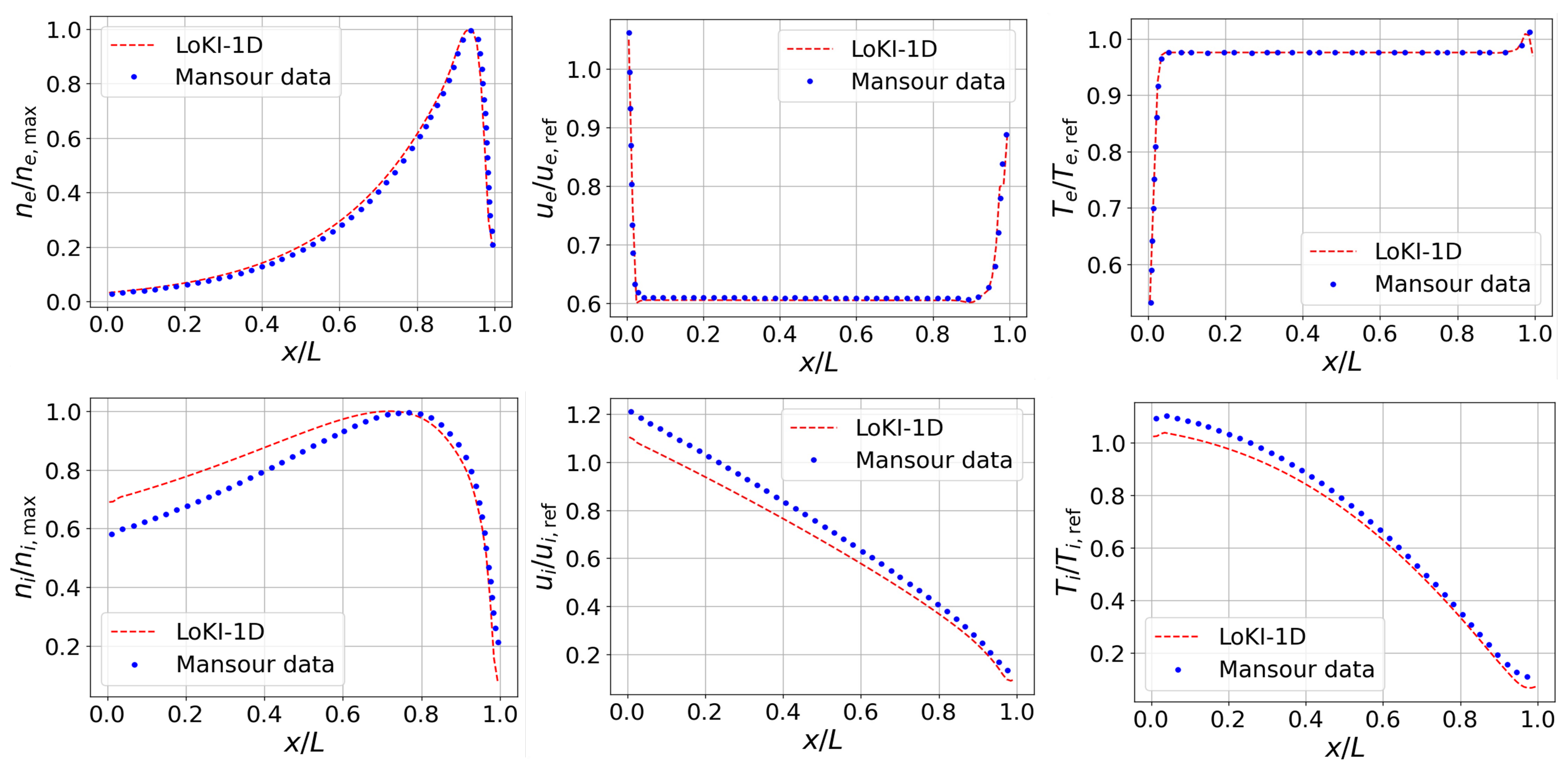
- Expected behaviour near cathode with agreement trends for different pressures;
- Creation of neutral and charged species early in the discharge.



Profiles of species properties and electric field evaluated at t = 12.4 µs (~4h computational time).

Model Benchmark [1]

- Goal: Validate the implementation of the **FFM model** for electrons and ions;
- Coupling with Boltzmann's equation solver LoKI-B [2] to obtain rate coefficients;
- Gas breakdown discharge in collisional regime: $pd = 50$ Pa · m, $V_b = 686.88$ V.



Benchmark: Density, velocity and temperature profiles obtained using the Full Fluid Moment model for electrons (above) and ions (below), compared with results from Mansour *et al.* [1].

Conclusions:

- **Successful FFM Implementation**: A 1D self-consistent Full Fluid Moment (FFM) model is successfully developed and validated through comparison against published results;
- **Kinetic Consistency**: The model tracked the complex discharge chemistry of CO_2 at early stages, resulting in the creation of new species starting from a pure CO_2 initial mixture;
- **Sheath Dynamics Capture**: The numerical framework correctly captures the physics of cathode sheath formation, showing a physically consistent potential drop leading to intense electric field growth and strong non-local electron heating.

Perspectives:

- **Plasma-Membrane Interface**: Implement plasma-membrane surface interaction, explicitly accounting for oxygen surface fluxes, surface kinetics and permeation through MIEC membranes;
- **Operational Assessment of CO2 Glow Discharges**: Evaluate CO_2 dissociation performance across DC and RF power regimes, comparing membrane-less and membrane-assisted reactor configurations, based on the works of Morillo-Candas *et al.* [8] and Dihya Sadi [9].

References:

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