Intensification of Hydrogen Flux in a Pd Membrane Separator and Membrane Reactor Under an Electric Field

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1. Introduction

High-purity hydrogen is required for fuel cell applications. Pd-based membrane reactors (MRs) are a promising technology enabling small-scale hydrogen production, by effectively separating hydrogen in-situ from a reacting gas mixture [1]. The rate of hydrogen permeation in MRs is the critical design parameter. It is affected by a range of factors, including temperature, pressure, and the presence of undesired byproducts (for example, carbon monoxide (CO)). The relatively strong binding energy of CO leads to the blocking of Pd adsorption sites and may result in a 30-60 % decrease in the transmembrane hydrogen flux, even at low concentrations [2].

Here, **electric fields are theoretically investigated as means to enhance the transport of H_2**, by lowering the binding energy of CO on Pd surfaces. This work studies the influence of applied electric fields (AEFs) on hydrogen flux within a Pd-based membrane separator and reactor.

2. Methods

We applied density functional theory (DFT) to calculate the adsorption energy of CO and hydrogen on Pd(111) under AEFs. Additionally, we have calculated the activation energy barriers associated with the hoping of H atoms within the Pd layers, under an electric field of various values (-0.8 V/Å < AEF < +0.8 V/Å). Our DFT calculations are based on the PBE exchange-correlation function within the Generalized Gradient Approximation [3] and projector augmented wave (PAW) method [4] implemented in the Vienna Ab Initio Simulation Package (VASP).

We have derived a one-dimensional model of a membrane separator and membrane reactor under an electric field in order to understand the effect of an electric field on the transport of hydrogen through the membrane. This is described by the modified Sieverts' law for the hydrogen flux, J_m proposed by Israni and Harold [2] which depends on the hydrogen surface coverage and free coverage:

$$J_m = (\theta_{H^*} + \theta_V) \cdot Q_m \cdot \left(\sqrt{P_{r,H_2}} - \sqrt{P_{p,H_2}} \right) \quad (1)$$

$$Q_m = A_m \cdot \exp\left(-\frac{E_m}{RT}\right) \quad (2)$$

$P_{r,\mathrm{H_2}}$ and $P_{p,\mathrm{H_2}}$ correspond to the hydrogen partial pressure in the retentate and permeate, respectively, while A_m and E_m are the pre-exponential factor and activation energy, respectively.

3. Results and discussion

The adsorption energy of CO increases with electric field strength from -0.8 to +0.8 V/Å. In contrast, the adsorption energy decreases for H_2 in the same range. A higher effect of the electric field on the CO molecule was observed, which is attributed to the difference in polarity of the molecules. Thus, **an applied electric field of -0.8 V/Å induces the desirable reduction of CO adsorption energy**

and enhancement of the adsorption energy of the H_2 molecule, which allows a reduction of CO coverage. In addition, the activation energy barriers.

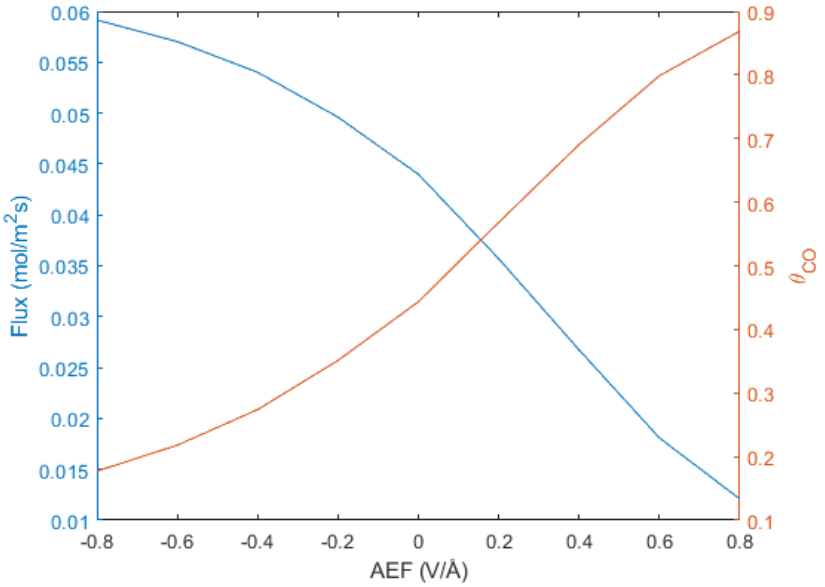

Figure 1. The CO coverage and hydrogen flux through the membrane along a separator under various electric fields ranging from -0.8 to 0.8 V/Å. The feed of the separator in the model is 30% hydrogen, 1% CO, 10 bar, and 600 ºC.

We will also report the calculated performance of methane steam reforming (MSR) in membrane reactors under AEFs, by accounting for the impact of AEFs on the kinetics of MSR. Intensification of the conversion and the pure hydrogen yield will be discussed.

4. Conclusions

In this work, DFT and a one-dimensional models of membrane separator and reactors are used to simulate the impact of electric field on H_2 flux. The results predict the **enhancement of up to 35% in the hydrogen flux through Pd membranes under a negative electric field**, by mitigating CO co-adsorption on the Pd surface.

References

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"Hydrogen", "Electric Field", "DFT", "Membrane Reactor"