

# ELECTROCHEMICAL PREFERENTIAL CO OXIDATION IN CO/H<sub>2</sub> MIXTURES: INFLUENCE OF NONLINEAR PATTERN FORMATION ON SELECTIVITY

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## Summary

The preferential oxidation of CO in CO/H<sub>2</sub> mixtures in a spatially distributed electrochemical membrane reactor is investigated. The reactor shows autonomous potential oscillations in space and time. The reason for this behavior is a cyclic interplay of the CO surface coverage and the anode electrode potential. The electric coupling of the reaction sites, mainly governed by the electrolytic conductivity, has a strong influence on the performance of the reactor. Three characteristic patterns are analyzed, which significantly differ in their integral selectivity. Furthermore, the influence of additional design and operating parameters is discussed.

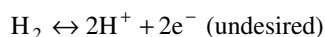
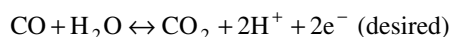
## Keywords

Hydrogen production, Membrane reactors, Dynamics and control of chemical reacting systems

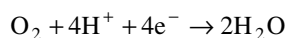
One of the key issues limiting the application of proton exchange membrane fuel cells is their susceptibility to traces of carbon monoxide within the hydrogen used as fuel. Carbon monoxide is produced in substantial amounts during the conversion of hydrocarbons to hydrogen-rich syngas. Typically, the fuel processor is coupled to or followed by a water-gas shift system, which reduces the CO content to a level of 1-3 vol%. In a subsequent removal step the CO content has to be decreased to tolerable levels of 10-30 ppm. Regarding this final purification step, the preferential oxidation (PrOx) of CO currently seems to be the most promising option for fuel cell systems with on-site hydrogen production.

Recently, Zhang and Datta [1] suggested a novel approach involving the electrochemical preferential oxidation (ECPrOx) of CO, which might have the potential to replace the PrOx in the above mentioned scheme. The main advantage, in comparison to the PrOx concept, is that non-selectively oxidized hydrogen is converted into electrical energy instead of being burned.

Anode reaction scheme:



Cathode reaction:



The design of such an ECPrOx reactor is similar to a PEM fuel cell. In contrast, instead of platinum, a platinum-ruthenium alloy is used as anode catalyst. When operated in the galvanostatic mode the reactor exhibits autonomous potential oscillations, which allow for a selective electro-oxidation of CO at relatively low overpotentials [1-3]. The reason for this behavior is a cyclic interplay of the CO surface coverage  $\theta_{\text{CO}}$ , which acts as an activator variable, and the anode overpotential  $\eta_{\text{A}}$ , which acts as the inhibitor variable [4] (Fig. 1).

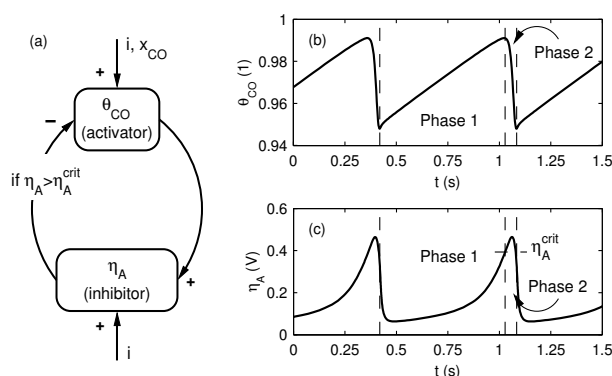


Figure 1. Two-phase mechanism to explain the autonomous potential oscillations of the system: (a) Graphic representation of the interplay between the key variables; (b) and (c) time evolution of the CO surface coverage  $\theta_{\text{CO}}$  and anode overvoltage  $\eta_{\text{A}}$ .

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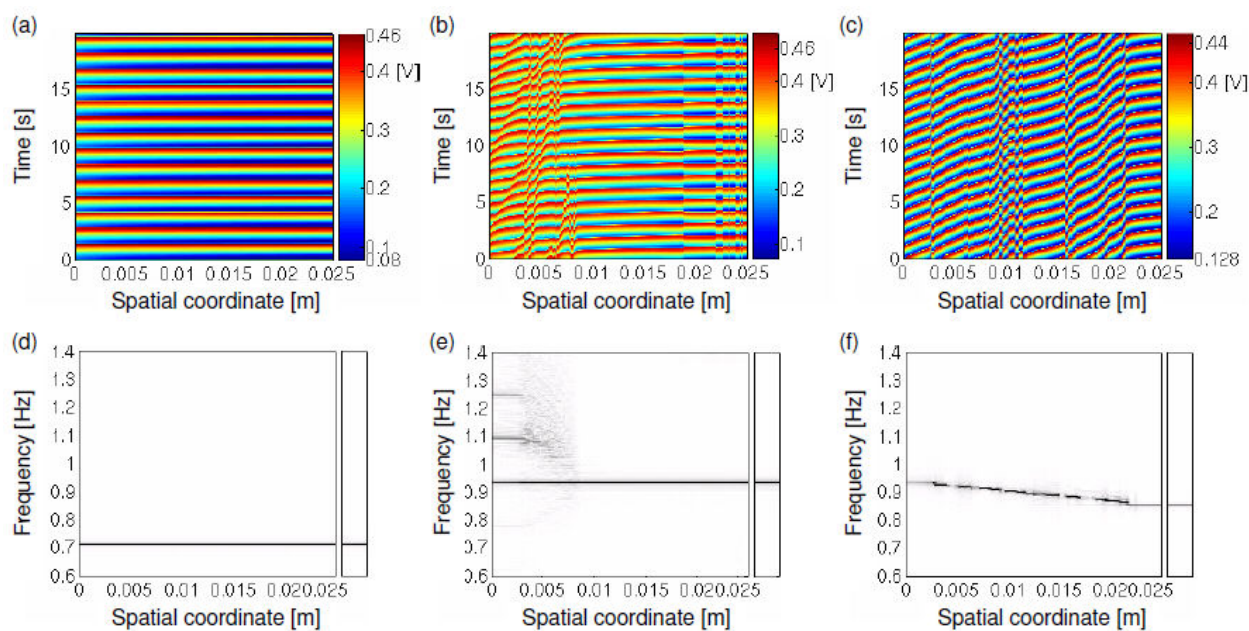


Figure 2. Influence of the electrolytic conductivity  $\kappa_e$  on pattern formation. Characteristic patterns for the anodic electrode potential (top row) and corresponding Fourier spectra (bottom row): (a,d)  $\kappa_e=5$  S/m, fully coupled pattern with the lowest selectivity; (b,e)  $\kappa_e=1$  S/m, partially coupled pattern; (c,f)  $\kappa_e=0.05$  S/m, fully decoupled pattern with the highest selectivity.

In our previous contributions [4-6], the gradient less system was investigated. It has been shown that the selectivity of oxygen towards  $\text{CO}_2$  is decreasing with increasing  $\text{O}_2$  conversion (i.e. with increasing cell current). This suggests either the use of a reactor cascade or the use of a spatially distributed reactor. For the cascade two different electrical configurations exist: (i) an electrical series connection and (ii) an electrical parallel connection of the reactors. While the former leads to a significant increase in the selectivity the latter does not [4,6]. As a reason for this behaviour rigid electrical coupling between the reactors, introduced by the electrical parallel connection, was identified. This coupling causes a synchronization of the single reactors, which leads to an enslavement of all the upstream reactors by the last reactor downstream the cascade [4].

In the present contribution, the behavior of the spatially distributed reactor is systematically analyzed. The above mentioned unfavorably electrical coupling is an intrinsic property of this system, which is introduced by the lateral electrolytic resistance. The upstream part of the reactor is therefore expected to exhibit a suboptimal performance, which is caused by an enslavement of the reactor's downstream part. With the help of a transient, isothermal 1d model we were able to theoretically confirm this expectation (Fig. 2(a)). The selectivity in this fully coupled regime is lower than the one in the case of a spatially distributed reactor without any electrical coupling.

In addition to the fully coupled regime, two other characteristic patterns were identified. With decreasing electrolytic conductivity, a partially decoupled and a fully

decoupled regime appear. In the fully decoupled regime (Fig. 2(c)), the oscillation frequency adjusts autonomously to  $\text{CO}$  mole fraction along the channel, which can be seen from the corresponding Fourier spectrum (Fig. 2 (f)). In contrast, the partially coupled pattern is characterized by a borderline (Fig. 2(b)). Downstream of this border, the reactor is coupled (Fig. 2(e)), while a local decoupling is observed upstream of the border. The selectivity in all three regimes differs, with the fully decoupled pattern having the highest selectivity.

Besides the electrolytic conductivity also other design and operating parameters influence the pattern type and with it the selectivity. In our contribution, we discuss the influence of the cell current, the  $\text{CO}$  inlet mole fraction and the flow rate of the feed gas.

## References

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