

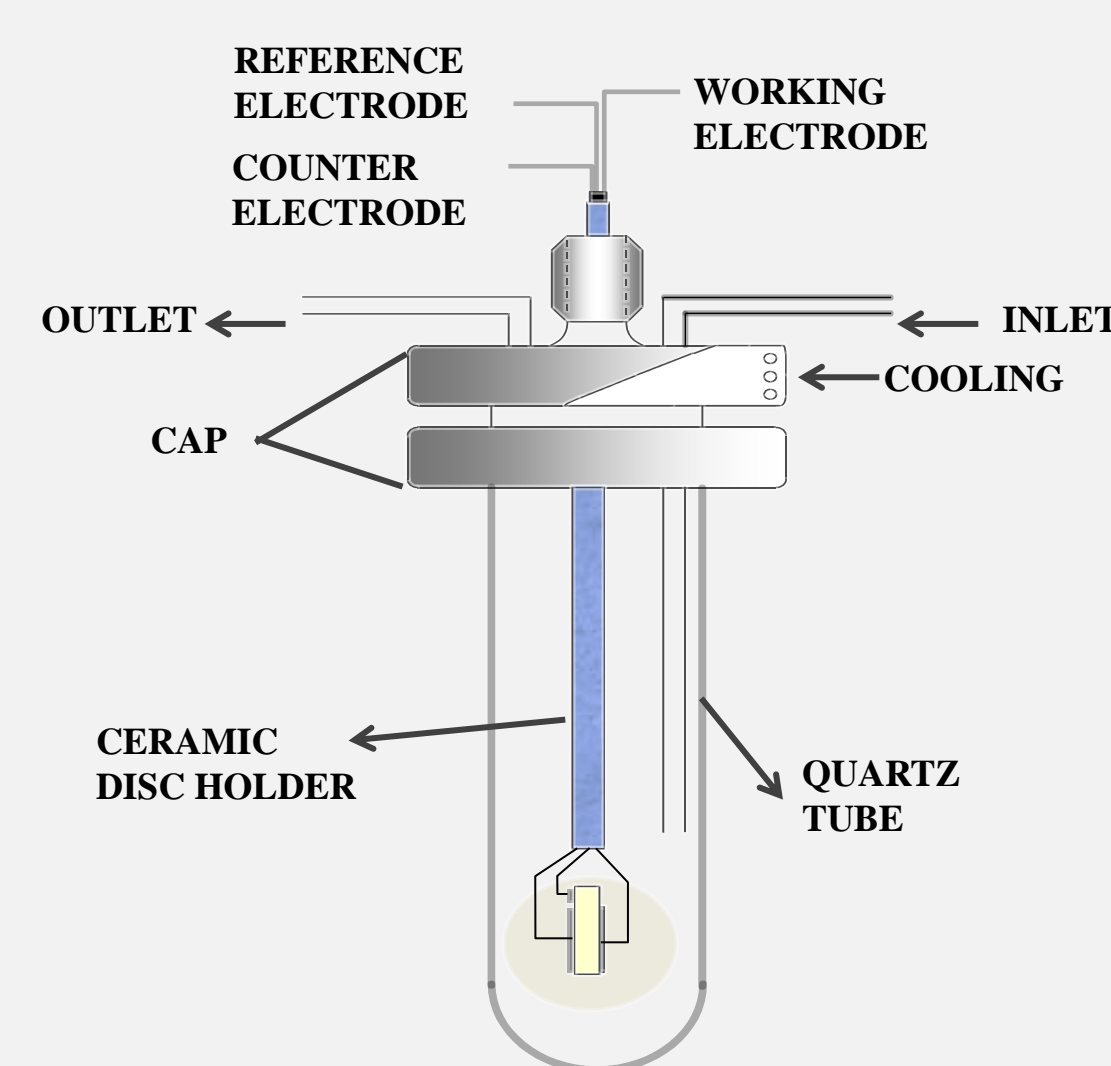
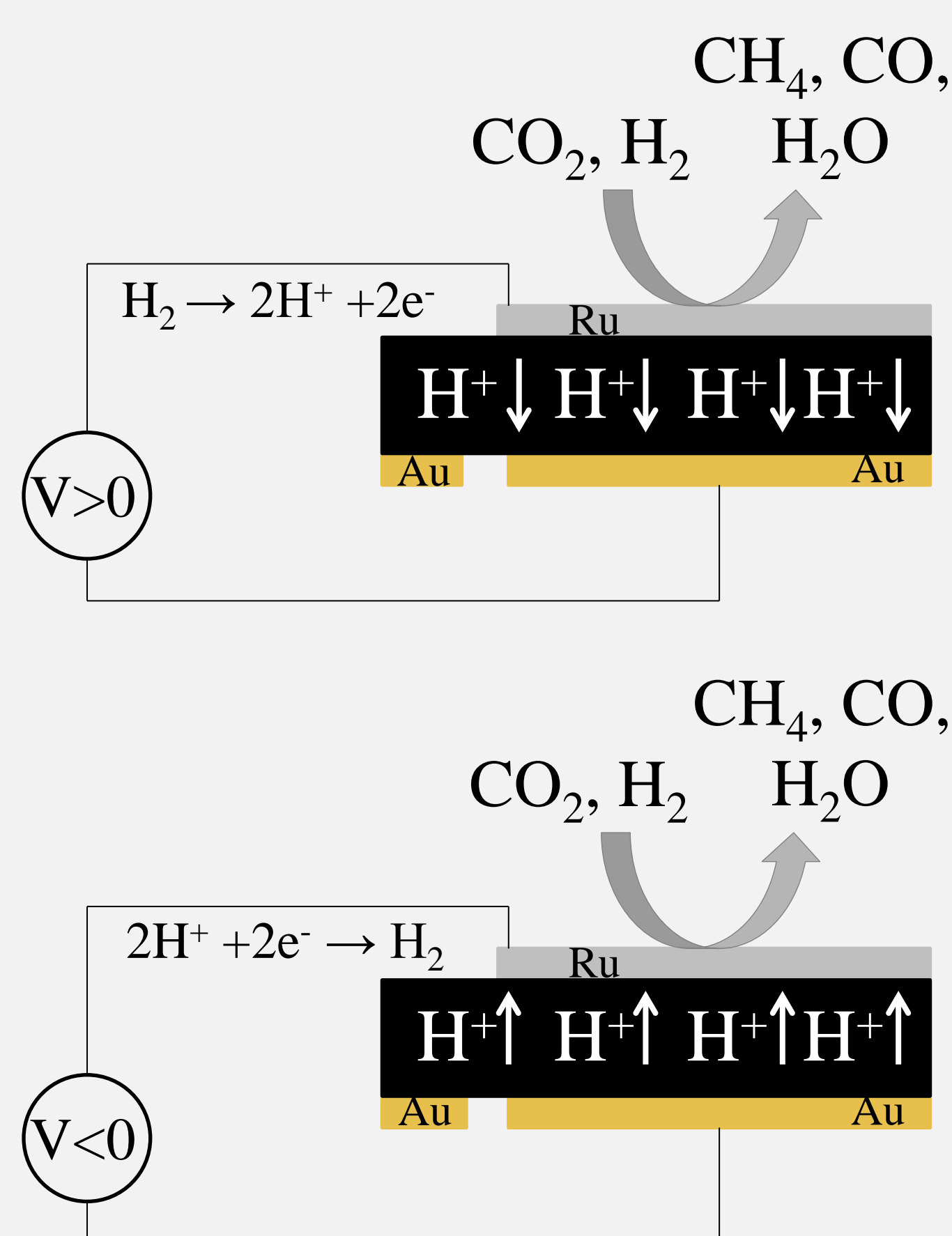
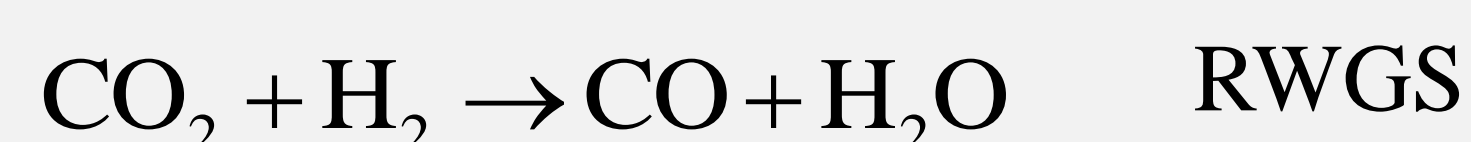
## Experimental

The hydrogenation of CO<sub>2</sub> to oxygenates and hydrocarbons is of significant technological and environmental interest. In this study the effect of Electrochemical Promotion of Catalysis (EPOC), or non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA effect), was used to reversibly promote the rate and selectivity of CO<sub>2</sub> hydrogenation reaction on Ru catalyst electrodes deposited on a BZY proton conductor. EPOC is due to electrochemically controlled migration of promoting or poisoning ionic species (H<sup>+</sup> in case of BZY) between the ionic or mixed ionic-electronic conductor and the gas exposed catalytic surface [1].

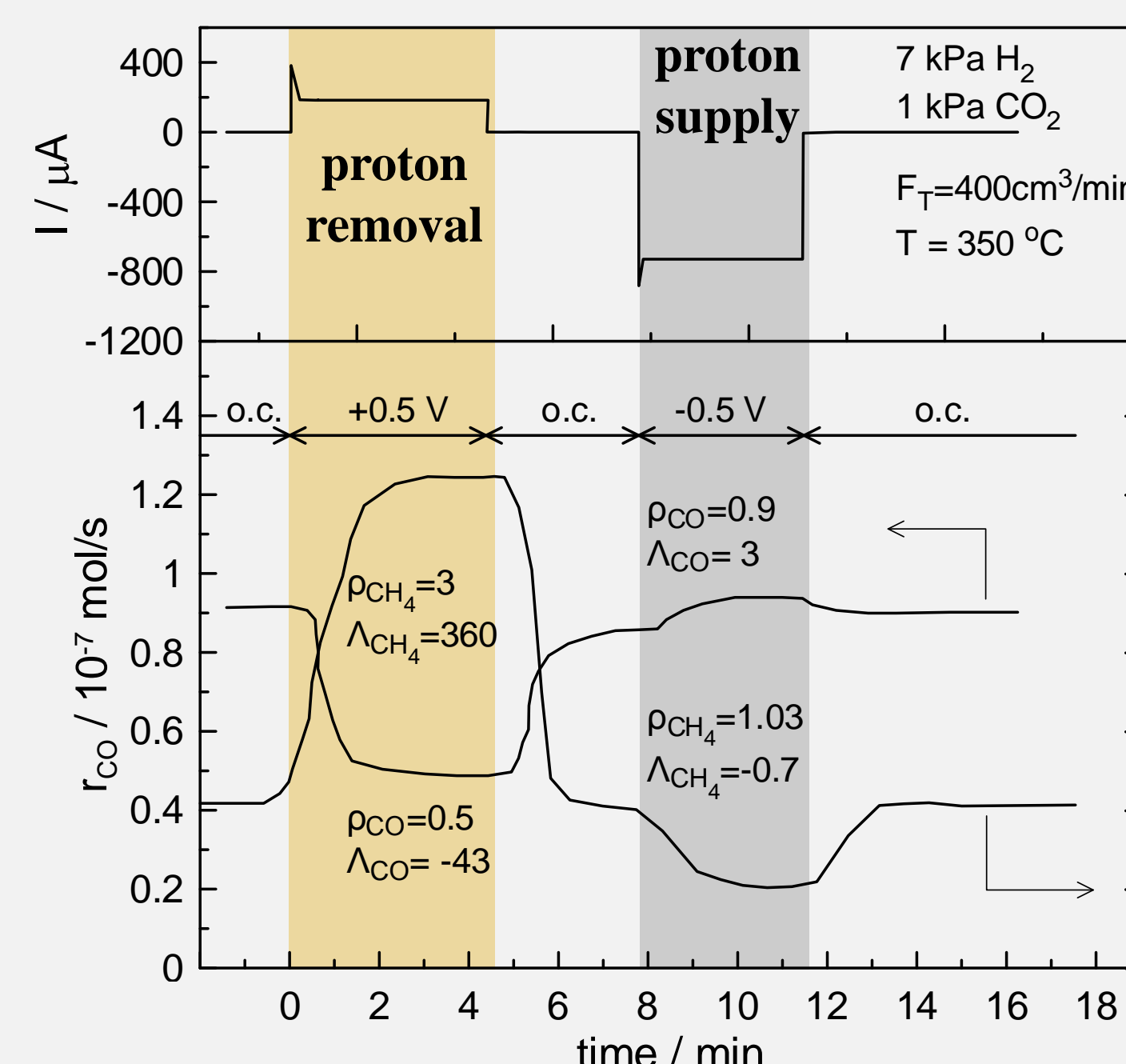
The catalyst Ru was deposited on a proton conductor, and served also as the working electrode. Gold counter and reference electrodes were deposited on the other side of the pellet. The catalyst-working electrodes were deposited by wet impregnation of metal chloride solutions. All samples were reduced at 450 °C in H<sub>2</sub> for 1hr.

The Ru/BZY/Au element was placed in a quartz reactor, (Figure 1) operating at temperatures 350 to 450 °C and atmospheric pressure. Constant currents/potentials were applied using a galvanostat-potentiostat. Feed reactant partial pressures were varied between 0.25 and 2.3 kPa for CO<sub>2</sub> and 1 to 15 kPa for H<sub>2</sub>.

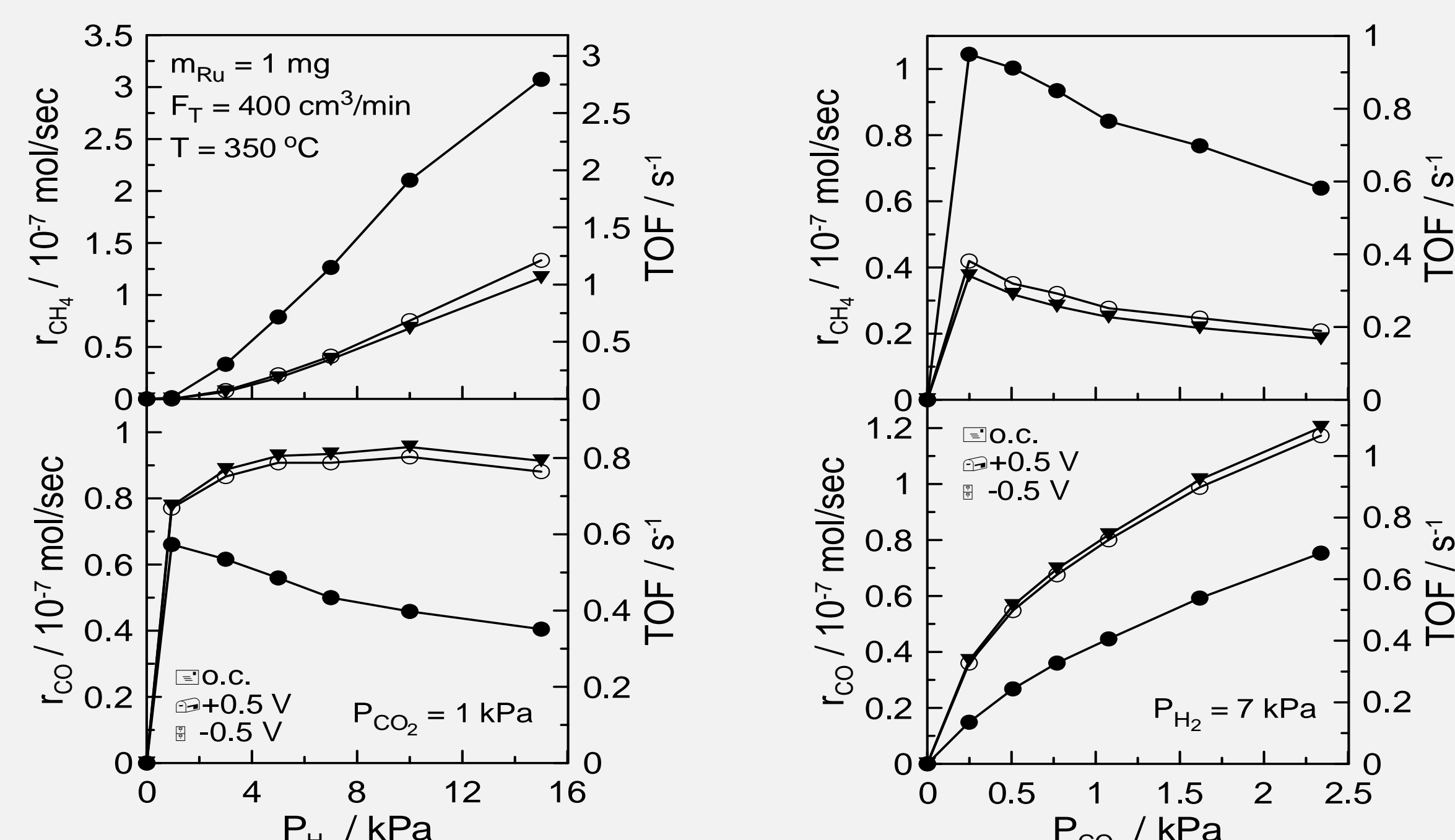
## **Results and Discussion**



**Figure 1:** Single chamber reactor used in EPOC studies [1].



**Figure 2:** Transient effect of constant applied positive and negative potential on the CH<sub>4</sub> and CO formation catalytic rates.



**Figure 3:** Steady state effect of the  $P_{H_2}$  and of the  $P_{CO_2}$ , on the rates of CO and  $CH_4$  formation under open circuit, positive and negative potential application.

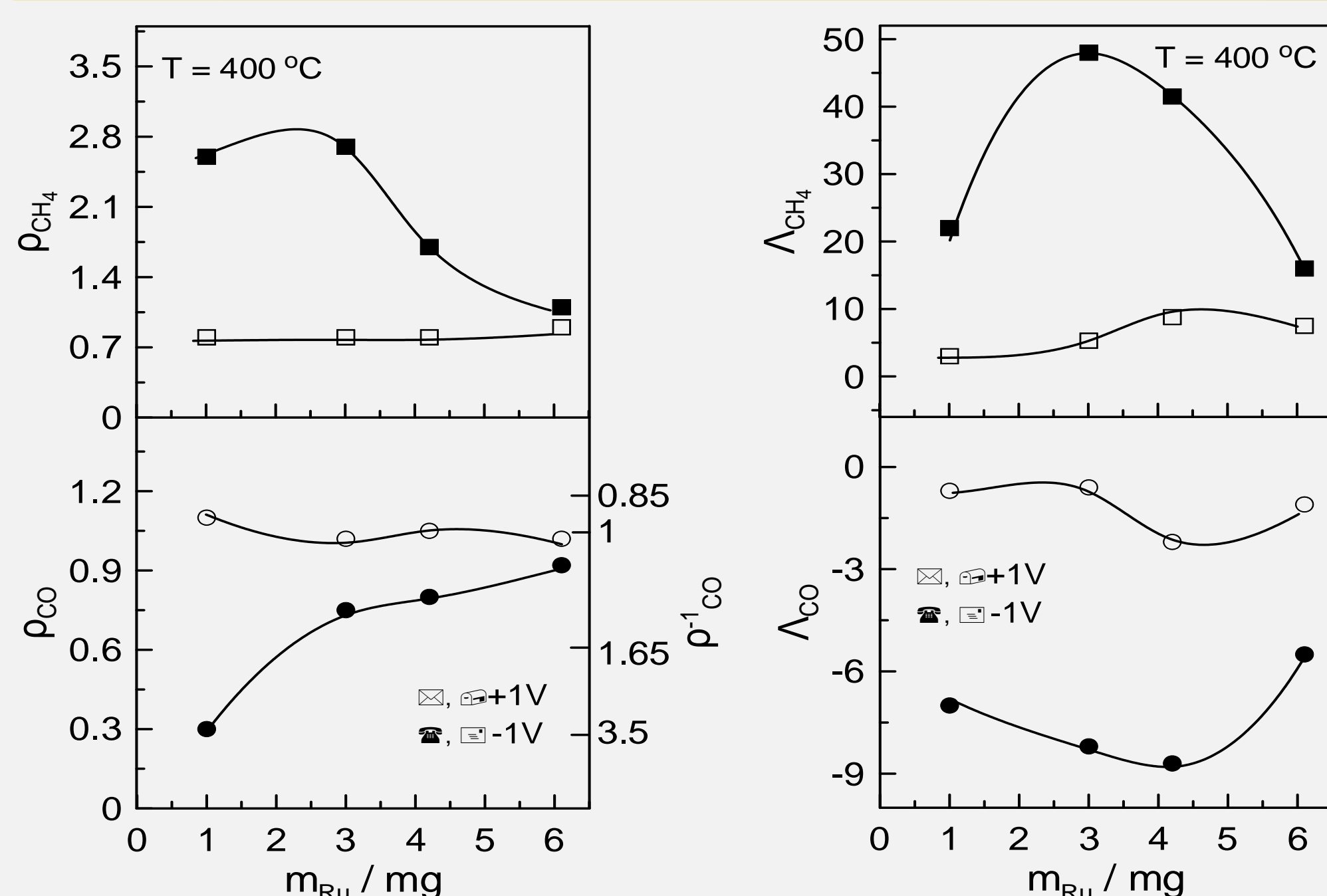
proton removal

enhances the hydrogenation to  $\text{CH}_4$  !  
 suppresses the formation of CO !  
 with large  $\rho$  and  $\Lambda$  values!

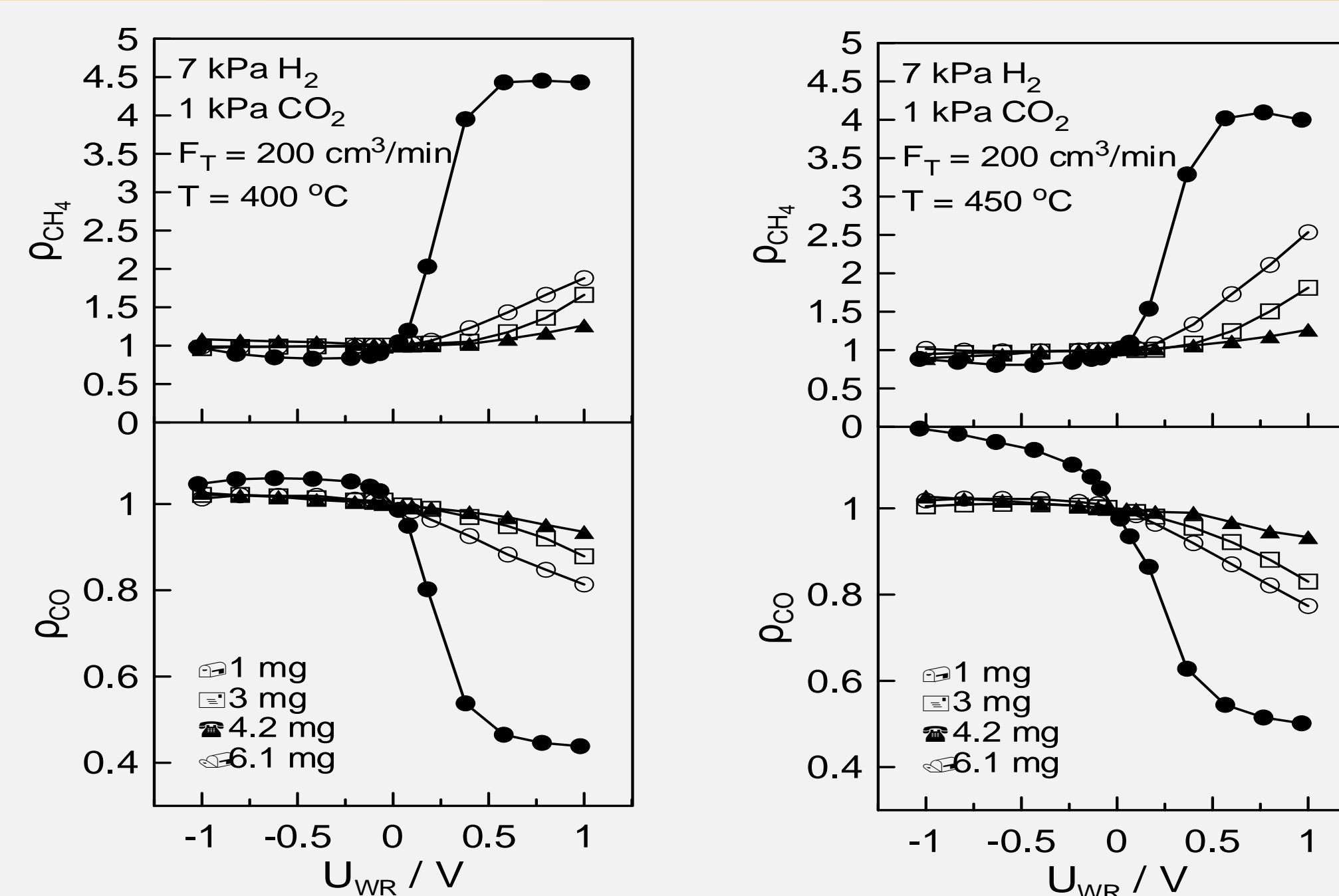
proton supply

has minimal effect on both rates

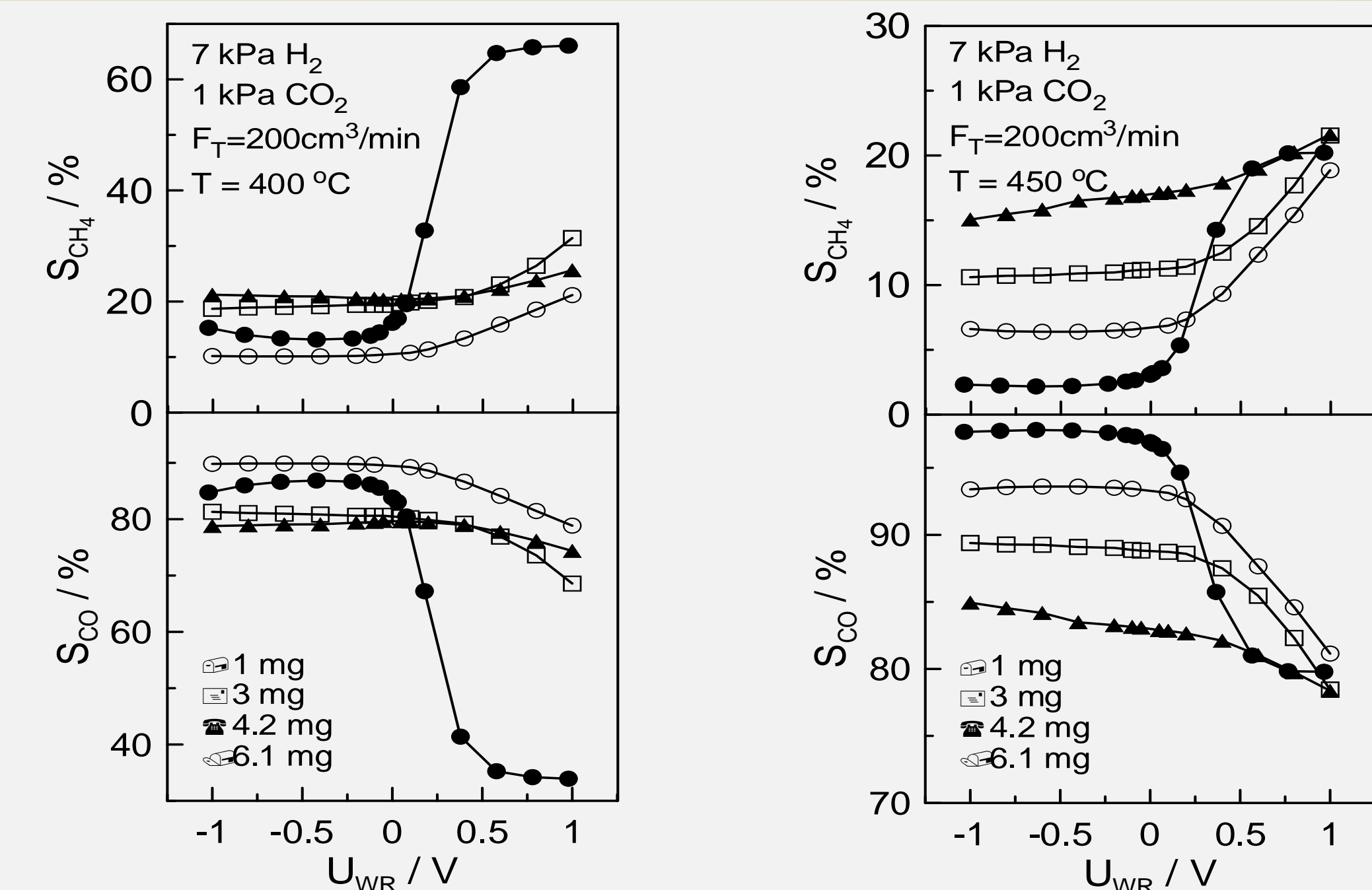
The observed electrophobic behavior ( $\partial r/\partial U_{WR} > 0$ ) for the methanation reaction and electrophilic behavior ( $\partial r/\partial U_{WR} < 0$ ) for the RWGS reaction is consistent with previous studies [2,3] and with the rules of chemical and electrochemical promotion [4].



**Figure 4:** Steady state effect of the metal loading on the rate enhancement ratio,  $\rho$ , and apparent Faradaic efficiency values,  $\Lambda$ , of CO and CH<sub>4</sub>.

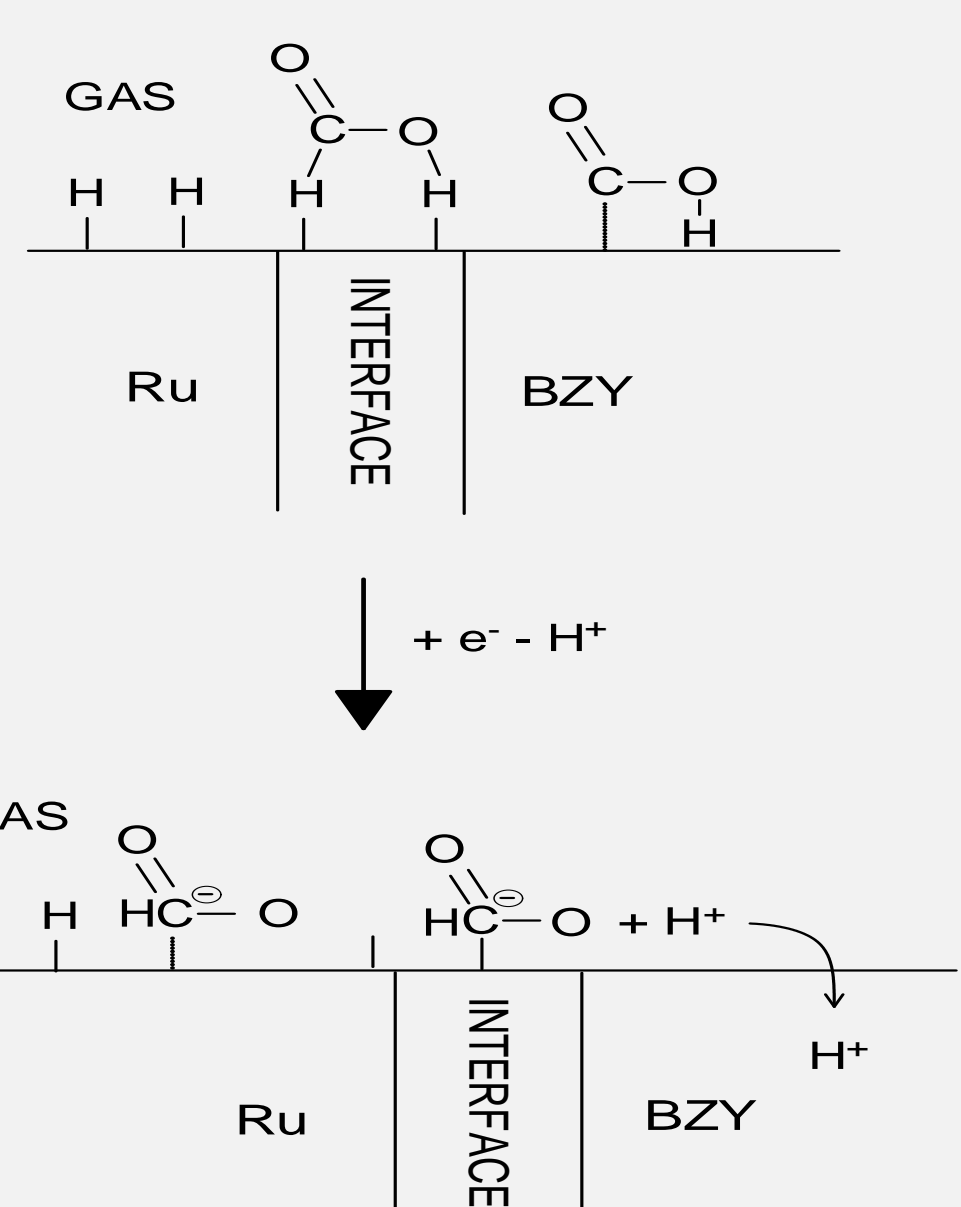


**Figure 5:** Steady state effect of the catalyst potential on the rate enhancement ratio,  $\rho$ , of CO and CH<sub>4</sub>, and on the metal loading.



**Figure 6:** Steady state effect of the catalyst potential on the selectivity of CO and CH<sub>4</sub>, and on the metal loading.

## **Conclusions**



**Figure 7:** Schematic of anionic promoter generation mechanism at the Ru/BZY interface.

- The observed kinetic and electropromoted kinetic behavior suggests that a promoting anionic species is generated at the metal/support, i.e. Ru/BZY, interface upon positive current application, i.e. upon proton removal from the catalyst into the BZY proton-conducting support.
- The importance of these interfacial adsorbed species is also manifested in the present system by the observed strong dependence of catalyst activity and selectivity not only on catalyst potential but also on catalyst loading and film thickness which strongly suggests the diffusion of a promoting species formed at the metal/support/gas three-phase-boundaries over the entire catalytically active metal/gas interface.
- It appears likely that this promoting anionic species is adsorbed formate anion obtained via electrochemically assisted deprotonation of formic acid adsorbed at the Ru/BZY interface, as shown schematically in Figure 7.

## **References**

- [1] C.G. Vayenas, S. Bebelis, C. Pliangos, S. Brosda and D. Tsiplakides, *Electrochemical Activation of Catalysis: Promotion, Electrochemical Promotion and Metal-Support Interactions*, (Kluwer Academic/Plenum Publishers, New York, 2003).
- [2] D. Theleritis, M. Makri, S. Souentie, A. Caravaca, A. Katsaounis and C.G. Vayenas, *ChemElectroChem* 1 (2014) 254-262.
- [3] D. Theleritis, S. Souentie, A. Siokou, A. Katsaounis and C.G. Vayenas *ACS Catalysis* 2 (2012) 770-780.
- [4] S. Brosda, C.G. Vayenas, J. Wei, *Appl. Catal. B: Environmental* 68 (2006) 109-124.

## **Acknowledgements**

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