

Macroscopic multi-dimensional modelling of electrochemically promoted systems[☆]



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HIGHLIGHTS

- We present new detailed 2- and 3-D macroscopic models of EPOC single-pellet systems.
- We estimate kinetic parameters of CO oxidation through optimization studies.
- We quantify the effect of the estimated parameters through sensitivity analysis.
- We investigate the effect of operating conditions through parametric studies.
- We quantify both the NEMCA and the Faradaic CO₂ production rate.

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ABSTRACT

The objective of this work is the construction of macroscopic models for electrochemically promoted catalytic systems, i.e. systems where the catalytic performance is improved by application of potential between the anode and cathode electrodes in the cell. This polarization effect leads to a formation of an effective double layer over the catalytic film due to migration of ‘backspillover’ species from the electrolyte to the working electrode when potential difference is applied in the system. In this paper, we propose a multidimensional, isothermal, dynamic solid oxide single pellet model, which describes the chemical and electrochemical phenomena taking place under polarization conditions. The electrochemically promoted oxidation of CO over Pt/YSZ is used as an illustrative system. The partial differential equation-based 2- and 3-dimensional macroscopic models that describe the simultaneous mass and charge transport in the pellet are constructed and solved in COMSOL Multiphysics. The model predicts species coverage on the catalytic surface, electronic and ionic potential curves across the pellet, gas mixture concentration within the reactor and CO₂ production rate. Parameter estimation is undertaken so as to provide us with values of parameters, which are necessary for the simulation of the model. Subsequent sensitivity analysis is performed to investigate the effect of the percentage change of each estimated parameter on the CO₂ production rate. As it is shown, the reaction rate curves obtained from the current modelling framework are in good agreement with values found in the literature.

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1. Introduction

The subject of this work is the development of accurate macroscopic models for electrochemically promoted catalytic systems. Electrochemical promotion of catalysis (EPOC), also referred to as non-Faradaic electrochemical modification of catalytic activity (NEMCA), is the enhancement of catalytic activity and selectivity as a result of an electrochemically controlled migration of “backspillover”

species, i.e. $[O^{\delta-} - \delta+]$, from the solid electrolyte to the catalytically active, gas exposed, electrode surface, when current or potential is applied between the two electrodes of the solid electrolyte cell. More specifically, oxygen anions are incorporated from the triple phase boundaries (TPBs), i.e. places where gas phase, catalytic film and electrolyte are in contact) forming BackSpillover Species (BSS) and then the BSS spill over the catalytic surface. Due to this migration, an effective double layer is formed over the catalytic film, which affects the binding strength of the chemisorbed reactants. Fig. 1 illustrates the effective double layer for a system of gaseous reactants (CO, O₂)/Metal (working electrode)/YSZ (solid electrolyte). The EPOC phenomenon was first observed in the early 1980s by Stoukides and Vayenas (1981) and has since been extensively studied experimentally and theoretically (Ladas et al., 1991; Metcalfe, 2001; Poulidi et al., 2011; Vayenas

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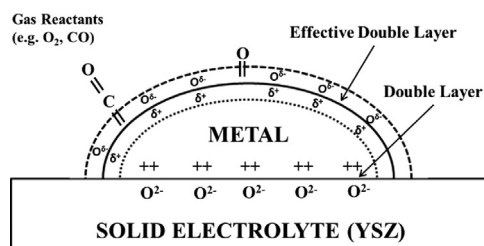


Fig. 1. Schematic of the effective double layer formation (Vayenas and Bebelis, 1999).

et al., 1990; Xia et al., 2010). However, few modelling studies have been performed describing the addressed effect, which were primarily focused on the catalytic surface kinetics. To the best of our knowledge, a systematic multi-dimensional modelling framework, which simulates the chemical and electrochemical phenomena taking place in electrochemically catalyzed systems and will allow robust system design, has not been formulated yet.

Stoukides and Vayenas (1981) have observed that the nature of a catalyst deposited on a solid electrolyte can be altered in a dramatic manner, when voltages are externally applied to the solid electrolyte cell. The study included ethylene oxidation on polycrystalline silver as catalytic reaction, at atmospheric pressure and temperatures close to 400 °C. It was observed that O^{2-} pumping from the electrolyte to the catalytic surface was taking place by applying voltage between the cathodic and anodic electrodes. This O^{2-} pumping phenomenon was found to result in an increase in the rate and selectivity of the heterogeneous catalytic reaction in a considerable and reversible manner. By the late 1980s, NEMCA was demonstrated for several catalytic reactions and was not limited to a specific solid electrolyte or catalyst (Vayenas et al., 1988, 1989; Yentekakis and Vayenas, 1988). It was shown that the work function of a catalyst can be altered when oxygen anions migrate from the solid electrolyte to the catalytic surface resulting in significant changes in the catalytic activity and as much as 4000% increase in the surface reaction rate. An enhancement factor, Λ ($\Lambda = \Delta r / (I/2F)$), was introduced to report whether the behaviour of the system was Faradaic or not (Vayenas et al., 1988). Here, Δr describes the polarization-induced change in the catalytic rate and $I/2F$ is the rate of supply/removal of oxygen anions (Faradaic rate) when electrical current, I , or a potential difference between the working and the reference electrodes is applied. A value of unity for Λ means that the behaviour of the system is purely Faradaic. Greater values signify non-Faradaic behaviour. Vayenas et al. (1990) have shown that the catalytic activity is exponentially dependent on the catalyst work function, which is in turn affected by polarization conditions in the cell.

The effect of EPOC was further studied giving insights of the surface dynamics of a catalytically electropromoted system (Ladas et al., 1991; Vayenas and Bebelis, 1997; Yentekakis et al., 1994). It was, moreover, found that the NEMCA effect was not limited to pure catalytic films, but it was also observed when dispersed (Marwood and Vayenas, 1998) or metal oxide (Wodiunig and Comminellis, 1999) catalysts were utilized. Ladas et al. (1991) established that just a small coverage of ions ($< 5\%$ of a monolayer) can change the work function of the catalyst without affecting the coverage of the rest chemisorbed species, while Yentekakis et al. (1994) observed that for Na coverages lower than 0.04, sodium was acting as promoter by increasing the surface reaction rate up to 600% and for greater than 0.04 Na coverage values, sodium acted as poison decreasing the rate by up to 90% due to the formation of a surface complex between CO, Na and Pt. Vayenas and Bebelis (1997) using X-ray photoelectron spectroscopy provided significant evidence that the normally chemisorbed oxygen, i.e. oxygen in the gas phase which is dissociatively adsorbed on the catalytic surface, was greatly more reactive than the

backspillover one. Marwood and Vayenas (1998) studied NEMCA in the case of a dispersed catalyst, Pt, on Au. It was observed that the NEMCA had the same features as in the earlier studied pure metal catalysts. Furthermore, Wodiunig and Comminellis (1999) used a metal oxide catalytic film, RuO_2 , and found that the O_2 desorption activation energy was getting lower by increasing the potential difference in the cell. This behaviour was completely reversible under current interruption.

Recently, Pliangos et al. (2000), Vayenas et al. (2003) as well as other research groups (Poulidi et al., 2007, 2011; Xia et al., 2010) have investigated the electrochemical promotion phenomenon, using novel configurations and bringing new challenges in the field of modern electrochemistry. Pliangos et al. (2000) investigated the NO reduction via dry impregnation with NaOH and found that the reduction rate was further increased by up to a factor of 20 under polarization conditions. Vayenas et al. (2003) have shown using scanning tunneling microscopy that the BSS can diffuse on the catalytic surface for greater than mm distances and thus the NEMCA effect could take place in commercial nm sized catalytic films. Poulidi et al. (2007) used a novel wireless configuration in a dual chamber reactor. More specifically, they have used a mixed protonic–electronic conductor as electrolyte to supply hydrogen promoting species on the catalytic surface (reaction side chamber) by manipulating the hydrogen chemical potential difference throughout the electrolyte. The adjustment of the chemical potential of hydrogen across the electrolyte was performed by utilizing hydrogen, helium and oxygen in helium as sweep gas (sweep side chamber). It was observed that the reaction rate could be increased by up to a factor of 1.6 only in the case of hydrogen as sweep gas and under certain conditions. This enhancement effect was completely reversible. Later, Poulidi et al. (2011) continued their wireless configuration studies utilizing a mixed oxygen ionic–electronic conductor as electrolyte in several experimental configurations. In this case, it was found that although there was an enhancement of the catalytic activity under oxygen utilization as sweep gas, the reaction rate did not return to its unpromoted state. Another novel configuration was developed by Xia et al. (2010). In this study, CO combustion was performed on a bipolar configuration of nano-dispersed Pt particles deposited on YSZ. Application of current was found to increase the reaction rate as much as 500 times. This non-Faradaic promotion effect was irreversible after current interruption.

As mentioned earlier, despite the great potential of modelling EPOC, as it will allow robust system design and thus the establishment of industrial-level applications, very few modelling studies have been performed so far. Vayenas and Pitselis (2001) developed a steady-state, 1D surface reaction–diffusion model to simulate NEMCA for a porous catalyst deposited on a solid electrolyte. In that study, BSS was the only species taken into account and the TPB was considered to represent the interface layer (with negligible thickness) between the porous catalytic film and the solid electrolyte. Furthermore, the BSS could be exorporated from the electrolyte and either diffuse through the catalytic film or react with the gas phase species. This model was used in Presvytes and Vayenas (2007) to study a system consisting of a semi-spherical catalytic particle interfaced with a larger YSZ one. The TPB, and thus the reaction zone, was extended over the entire thickness of the catalytic particle. An effectiveness factor was used to determine the catalytic performance. It was found that the catalytic particle geometry has a minor effect on the catalytic performance. Foti et al. (2002) formulated a model to describe the reaction rate transients of an electrocatalytically promoted system. Fast diffusion of BSS, which could form on the catalytic surface if and only if there were free active surface sites, on the catalytic surface as well as a first order BSS consumption rate were considered. It was found that the BSS coverage on the catalytic surface was

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