

Transient Kinetic Modeling of Hydrocarbon Oxidation on Pt-Ceria Anodes by the Anode Transport and Reaction Process Model

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A major advance in the pursuit of a commercially feasible fuel cell is development of a direct hydrocarbon solid oxide fuel cell (SOFC) with broad fuel flexibility. With complex fuels come complex surface reactions, the nature of which must be understood in efforts to develop effective electrocatalysts [1–5].

Catalytic and electrocatalytic oxidation of C_7H_8 and CH_4 were studied on a gadolinium-doped ceria (CGO) anode with either Pt or PtPd catalytic modifiers. The electrolyte was CGO for C_7H_8 and yttrium-stabilized zirconia (YSZ) for CH_4 , and the cathode was lanthanum strontium cobalt (LSC) in both cases. The experiments were performed in a dual chamber system in which the anode side of the SOFC chamber was connected to an ultrahigh vacuum (UHV) chamber. Concentrations and temporal responses of reacting species were monitored in the UHV chamber with a Balzers 112 mass spectrometer.

Figure 1 shows the response of toluene oxidation to a step change in oxygen ion current. Upon the onset of oxygen ion current (red line) at 10 min, a large increase in oxidation occurs (solid line), above the catalytic steady state value at time zero. The oxidation current passes through a maximum at about 20 min and decays gradually until the oxygen ion current is turned off at 84 min.

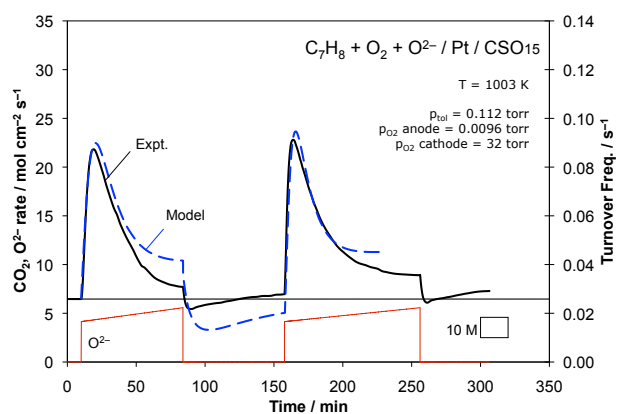


Figure 1: Response of toluene oxidation (solid line) to a step change in oxygen ion current (red line) for reaction on a Pt/CSO anode. The dashed line shows the result of the ATRP model. The box shows $10M$, where M is the number of reaction sites on the Pt surface. See text for fitting details.

The complex reaction behavior was modeled with an anode transport and reaction process (ATRP) model that accounts for both oxygen ion transport in the electrolyte and catalytic reaction kinetics. Figure 2 shows a surface reaction schematic of the model. Oxygen ions transported

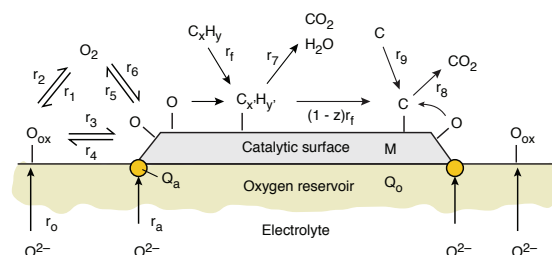


Figure 2: Schematic of surface reactions in the ATRP model. See text for further details.

through the electrolyte may adsorb with discharge at the metal (Q_a) or become part of the oxygen reservoir (Q_o) by formation of cerium oxide at the anode. Hydrocarbon adsorbs and reacts through reactions r_f, r_7-r_9 . Oxygen exists in three-way equilibrium among gas phase, adsorbed on the metal, and oxide through reactions r_1-r_6 . Carbon generation, whether by gas phase or surface processes, forms islands that block reactive sites. The model has at least 7 adjustable parameters, though the most significant ones are the size of the oxygen reservoir Q_o and the fraction of its capacity q , varying from 0 (empty) to 1 (full).

The dashed line in Fig. 1 shows the best fit obtained for the data, which reproduces all features with semi-quantitative agreement. On the basis of the model, the experimental results can be interpreted as follows. At the onset of oxygen ion current, the oxygen reservoir ($Q_o/M = 10$, where M is the number of reaction sites on the Pt surface), has an activity of $q = 0.1$. At the onset of oxygen ion current oxidation increases, by removal of surface carbon, and consumes oxygen to draw down the reservoir. When the reservoir is depleted, reaction decays until approximately the steady state value, at which time $q = 0.02$.

By specifically accounting for oxygen transport to the anode catalyst and the coverage of surface carbon, the ATRP model can simulate a variety of transient and periodic reaction processes in solid oxide surface chemistry.

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