



# Phosphine induced Nickel Migration in SOFC Anodes: A Computational Study



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## ABSTRACT

The poisoning of anode materials by impurities in coal syngas is a significant problem for utilization of coal syngas in Solid Oxide Fuel Cells (SOFCs). One such impurity, phosphine is known to cause catastrophic failure of SOFC anode at ppm level concentrations. A significant phenomenon observed in SOFC anodes, made of Ni-YSZ cermets, when exposed to phosphine is migration of the nickel from porous matrix towards the surface, which is believed to be one of the reasons for performance degradation. The mechanisms responsible for the experimentally observed nickel migration are not well understood. In this study, a plausible mechanism is proposed to reveal the effect of electrical current and steam concentration on nickel migration in SOFC anodes. A physics based transport model for nickel migration is formulated based on the electro-migration, formation of the secondary phases and diffusion. This model is integrated into a readily available one dimensional in house code for predicting SOFC anode degradation due to fuel impurities. Simulations show that the proposed mechanism of Ni diffusion driven by secondary phase formation, the electrical force, and humidity can reveal the experimentally observed accumulation of Ni and secondary phases on the SOFC anode surface.

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## 1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical devices which are operated at elevated temperatures (700 °C–900 °C) with various fuels including gasified coal (syngas). Utilization of coal syngas in SOFCs can play a critical role in future power generation, with much less environmentally harmful emissions than conventional coal combustion [1]. However, the inherent contaminants found in coal syngas such as phosphorus, antimony, arsenic, zinc, sulfur, mercury, selenium, and vanadium may degrade the performance and durability of SOFC significantly even at low ppm levels [2]. The standard SOFC's anode composition is Ni-YSZ cermet which is affected by coal syngas contamination during cell operation. The effect of gasified coal contaminants on the Ni-YSZ anode, thus on the performance and durability of SOFCs has been an important research subject [1–3]. A significant phenomenon in SOFC Ni-YSZ cermets anodes exposed to phosphine is migration of the nickel from porous matrix to the surface, which is believed to be one of the reasons for performance degradation [1,4,5]. The performance degradation and/or Ni migration of Ni-YSZ anode due

to the phosphine in syngas at low level (ppm levels) has been investigated by many researchers. Demircan et al. [4] reported the possible mechanism of phosphine induced performance degradation with two different mechanisms: (i) The loss of Ni in the active layer of the anode via nickel migration from anode active layer to the anode surface (ii) the production of Ni-P compounds decrease the number of active sites in Ni catalyst. Xu et al. [5] reported that, Ni can react with phosphine under cell operation conditions and form a liquid nickel phosphide phase which may possibly increase Ni migration from active layer to anode surface. Lussier et al. [1] reported a similar mechanism for Ni migration for hydrogen sulfide exposure. In addition to the formation of Ni-P phases, it has been reported that moisture content in the fuel and the electrical current also affect the nickel accumulation at anode surface [6–8]. Zhi et al. [6] and Silva [8] had investigated the effect of the current on the nickel transport. They reported that the one possible cause of the nickel accumulation under the applied current at the anode surface is the electro migration. Celik et al. [7] run the cell under different applied current and steam concentration. It was observed by Celik et al. that both applied current and steam concentration accelerated the nickel transport towards the anode surface. However, the mechanism responsible for the experimentally observed Ni migration is still not well understood. The steam concentration has a direct effect on the electro migration [9] and

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the formation of the secondary phases [7,10,11]. Therefore, the formation of secondary phases and the electro migration due to the applied current seem to be the most reasonable mechanisms, which are possibly responsible for nickel migration.

Formation of secondary phases has been investigated by different groups. Lussier et al. [1] and Demircan et al. [4] observed that the chemical compound on anode surface can be Ni and Ni compound with impurities such as  $H_2S$  and  $PH_3$ . Marina et al. [12] reported that the most possible species of Ni-P compounds are  $Ni_3P$ ,  $Ni_5P_2$ ,  $Ni_{12}P_5$ , and  $Ni_2P$ . Nickel conversion to nickel phosphide in the anode was considered to be one possible mechanism of SOFC performance degradation by Marina et al. [12]. Guo et al. [11] investigated the possible secondary phases formed due to phosphine exposure. Guo et al. [11] observed the formation of secondary phases inside the anode and the dominant P-based phases were found to be nickel phosphates such as  $Ni(PO_3)_2$  for a cell under load (e.g. 0.3 V), however under open circuit voltage (OCV) condition the most possible secondary phase was found to be  $Ni_3P$ .

Electro migration has been recognized as an important mechanism which may lead to failure in electrical and electronic systems [9,13,14]. Electro migration was suggested to be one of the responsible mechanisms for the redistribution of elements in the Ni-YSZ SOFC anode under applied current [6,15].

Based on the information found in the literature, we postulate that the nickel concentration gradients inside the anode could potentially cause Ni diffusion. Upon phosphine exposure, the Ni on the surface layer is the first to react and form secondary phases causing the Ni concentration to decrease further at the surface. This will drive the diffusion of Ni from the bulk of the porous anode to the surface. The melting point for some secondary phases that are reported by Marina et al. and Guo et al. [11,12] is close to the usual cell operating temperature of 800 °C causing them to soften and thus be more conducive for Ni migration. The effect of the current can be approximated as a convective term included by the electro migration mechanism as explained by Popovich et al. [16] for electrical and electronic systems.

Along these lines, a transport model for nickel migration is formulated and it is integrated with an existing one dimensional code [17] for predicting SOFC anode degradation due to fuel impurities. Interested readers are referred to [2,17] for detailed information about 1D degradation model. In this work, an attempt is made to understand the elemental redistribution within the

SOFC anode under  $PH_3$  exposure and the mechanism of Ni migrations by performing simulations at different current loading conditions. In addition, simulations were performed on SOFC anode to understand the influence of the steam concentration on the Ni migration phenomena.

## 2. Theory and Model Equations

### 2.1. Integration with one Dimensional Degradation Model

A transport model developed to predict fuel contaminant induced elemental redistribution in SOFCs anodes is integrated into the one dimensional impurity induced degradation model developed by Cayan et al. [17]. The degradation model employed in this work considers the competitive adsorption of hydrogen and the phosphine on the nickel catalyst surface inside the anode. Detailed information on the performance degradation model can be found in Cayan et al. [17]. The dependency of anode porosity and electrical conductivity as well as the exchange current density of hydrogen to local contaminant coverage is given as follows, [17,18];

$$\varepsilon = \varepsilon_0(1 - 0.95\theta^p) \quad (1a)$$

$$\sigma = \sigma_0(1 - 0.95\theta^q) \quad (1b)$$

$$i_0H_2 = c_1 \left( \frac{y_{H_2,int}}{y_{H_2,ref}} \right) \exp\left( \frac{E_{act,H_2}}{R_u T} \right) (1 - \theta_{Ni-PH_3,int}^m)^n \quad (2)$$

Where  $\varepsilon_0$ ,  $\sigma_0$ ,  $\varepsilon$ ,  $\sigma$  and  $\theta$  are initial porosity, initial conductivity, porosity, conductivity and phosphine coverage, respectively. In Eqs. (1) and (2), p, q, m and n are the model parameters obtained by calibration of the model against available experimental data for button cells. The constant  $c_1$  is taken as  $3.94 \times 10^7$ , the hydrogen reference concentration,  $y_{H_2,ref}$ , is 0.33, the hydrogen activation barrier,  $E_{H_2,act}$  is 91.7 kJ/mol [2], and  $Ni-PH_3, int$  is the phosphine coverage at the anode/electrolyte active interface.

The newly developed nickel migration model is composed of three parts (Fig. 1), formation of secondary phases, species diffusion and transport by electro migration. The first part, formation of secondary phases, is interlinked with transport of contaminant coverage which is calculated from one dimensional degradation

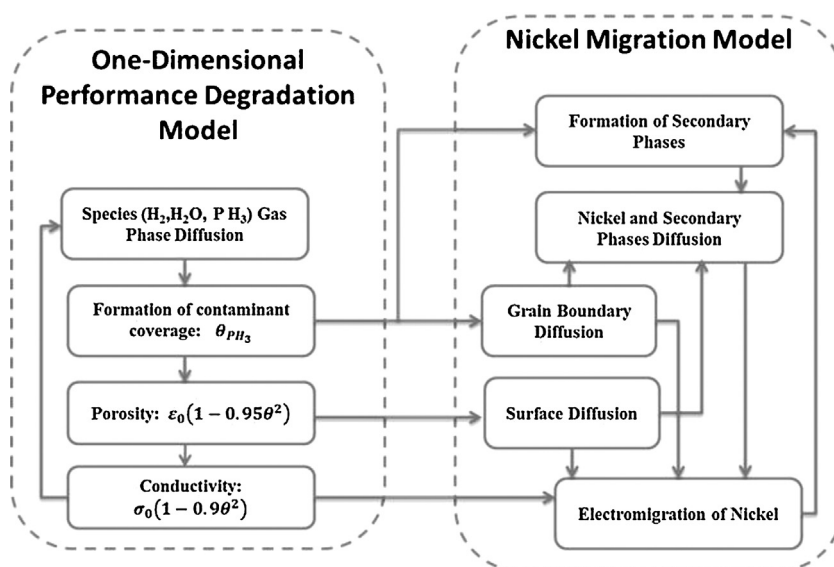


Fig. 1. Integration of nickel migration and one dimensional performance degradation code.

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