

The Pt/Nafion/Air Triple Phase Boundary: Model,  
Experiment, and Implications for PEM Fuel Cells  
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The idea of the *triple phase boundary* (TPB) is extensively employed in the fuel cell literature, especially with respect to solid oxide fuel cells (SOFCs) and polymer electrolyte membrane fuel cells (PEMFCs). The TPB concept holds that the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) can only occur at confined spatial sites, called “triple phase boundaries” where electrolyte, gas, and electrically connected catalyst regions contact. A simplified schematic of the TPB is shown in Fig. 1. The reaction kinetics (especially the ORR kinetics) often present a significant limitation to fuel cell performance. Therefore, understanding, characterizing, and optimizing the TPB content in fuel cells provides excellent opportunities for performance enhancement.

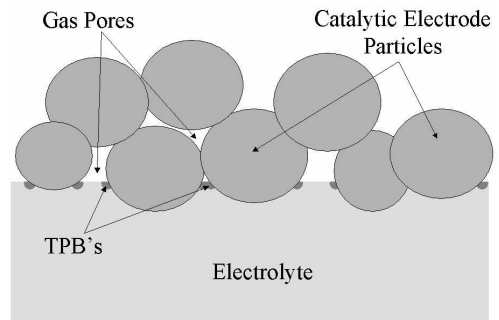
From a scientific perspective, several recent efforts have been made to more clearly delineate the nature and properties of the TPB. Most of this work has focused on SOFC's [1-3]. In contrast, very few studies have considered PEMFC systems [4]. However, in all cases, there is a growing realization that the simple concept of the TPB as a singularity is unrealistic; rather, it should be thought of as a “zone”, whose width, properties, and behavior depend on a complex interplay between coupled reaction and diffusion processes. (See Fig. 2)

In this presentation, we develop a mathematical model which seeks to describe the nature, properties, and scaling of the TPB for a Pt/Nafion PEMFC system. As a general framework, the model is applicable to both SOFC and PEMFC systems; minor changes are required for application to SOFCs. Fig. 3 shows example concentration profiles predicted by the model along a catalyst/electrolyte interface. The shapes of these concentration profiles are largely determined by a dimensionless length parameter  $ha$ , which relates the kinetic length scale of the system ( $1/h$ ) to the real length scale of the system ( $a$ ). From this dimensionless length parameter, we can arrive at a definition for an “effective TPB width”,  $w_{TPB} = 1/h$ .

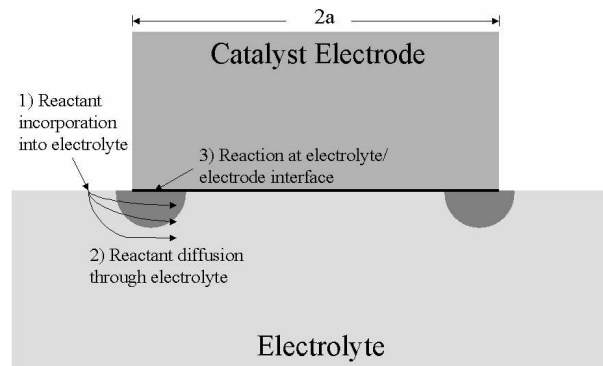
Using the model and our definition of the TPB width, implications for PEMFC catalyst layer design are explored. Additionally, scaling predictions of the model are compared to kinetic observations from geometrically well-defined Pt-microelectrode/Nafion experiments, and are shown to match closely. (Fig. 4)

#### References

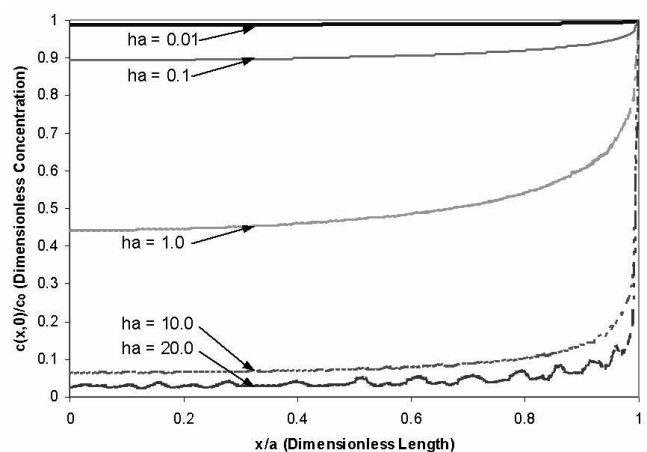
- [1] J. Mizusaki, H. Tagawa, K. Tsuneyoshi, and A. Sawata. *Journal of the Electrochemical Society*, 138(7), 1991.
- [2] J. Fleig. *Annual Review of Materials Research*, 33(1), 2003.
- [3] A. Bieberle, L. P. Meier, and L. J. Gauckler. *Journal of the Electrochemical Society*, 148, 2001.
- [4] R. O'Hayre and F.B. Prinz. *Journal of the Electrochemical Society*, 151(5), 2004.
- [5] R. O'Hayre, F. Gang, W. D. Nix, and F.B. Prinz, *submitted, Journal of Applied Physics*



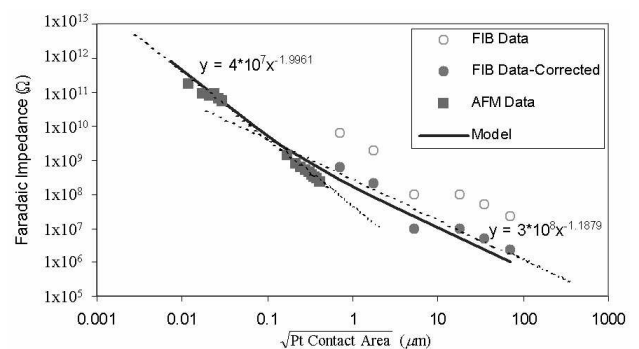
**Figure 1:** Simplified diagram of the electrode-electrolyte interface in a fuel cell, illustrating the triple phase boundary reaction zones where the catalytically active electrode particles, electrolyte phase, and gas pores intersect.



**Figure 2:** Our simple TPB model, showing the physical processes governing the nature and properties of the TPB.



**Figure 3:** Dimensionless concentration profiles  $[c(x,0)/c_0]$  versus dimensionless length  $[x/a]$  for various values of  $ha$ . Profiles derived from the TPB model.



**Figure 4:** Faradaic impedance ( $R_f$ ) versus Pt/Nafion contact size for FIB-patterned Pt/Nafion microelectrode [4] experiments (●) and Pt/Nafion AFM point contact [5] experiments (■). Dashed lines (---) are power law fits to the data; they denote a change in slope from -1 to -2, indicating a transition from perimeter based scaling to area based scaling. This transition is predicted by the TPB model (—).