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A comprehensive study on effective triple-phase boundary density and its correlation with active anode thickness in solid oxide fuel cells

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Abstract

Solid oxide fuel cells (SOFCs) are highly promising devices for efficient and low-emission energy conversion. The effective triple-phase boundary (TPB) density refers to the fraction of percolated TPB density that effectively contributes to the current production during cell operation. This is one of the most fundamental and least understood aspects of the cell design and performance assessment. This study methodically investigates the effective TPB density, using a computational fluid dynamics model based on the TPB-based kinetics and its correlation with the active anode thickness. Experimental data from previously published studies with varying thicknesses of anode functional layer and operating regimes are utilized to validate the model. The results of this study reaffirm that a significant fraction of the percolated TPB density in SOFCs remains unused during cell operation. This finding emphasizes the need to consider the effective TPB density for theoretical and experimental investigations focusing on optimizing cell performance. Furthermore, an inverse relationship is observed between the effective TPB density and the active anode thickness; a lower active anode thickness corresponds to a higher effective TPB density and vice versa. These findings contribute to advancing sustainable energy systems by guiding the development of more efficient SOFC designs and operational strategies that effectively utilize TPB sites.

KEYWORDS

active anode thickness, effective TPB density, hydrogen oxidation, Ni-YSZ, TPB-based kinetics

Abbreviation: CFD, computational fluid dynamics; GDC, gadolinium-doped ceria; MIEC, mixed ionic electronic conducting; OCV, open circuit voltage; RDS, rate-determining step.

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1 | INTRODUCTION

The world is currently experiencing an energy crisis as a result of the depletion of conventional fossil fuel resources and the negative environmental consequences of their use. Consequently, there has been a rise in the need for environmentally friendly and renewable energy resources and technologies, leading to the emergence of solid oxide fuel cells (SOFCs) as a viable and promising alternative. These fuel cells can utilize fuel sources such as hydrogen, natural gas, and biofuels, transforming them into electricity through electrochemical reactions.¹ Additionally, SOFCs are appealing due to their high efficiency, fuel adaptability, and relatively high operating temperature, which render them suitable for a variety of applications, including transportation and combined power and heat generation.² A standard SOFC consists of a compact ceramic electrolyte positioned between an anode and a cathode. The anode promotes oxidation reactions, while the cathode facilitates reduction reactions. In contrast, the electrolyte conducts oxide ions. Multiple ceramic-metal composite anodes, also known as cermet anodes, have been designed for different types of fuels and operating conditions.³ The most commonly found cermet anode is composed of nickel and yttria-stabilized zirconia (Ni-YSZ) because of its exceptional electrochemical activity and operational stability.⁴ The Ni–YSZ cermet comprises three distinct phases: Ni, YSZ, and pore phases. The gaseous fuel diffuses through the pores, whereas electrons and oxygen ions move through the Ni and YSZ phases, respectively. The electrochemical oxidation process takes place at the triple-phase boundary (TPB), which is the interface between the three phases. This reaction produces both current and reaction products.⁵ The efficiency of the fuel cell is strongly dependent on the competence of the multiphysics phenomenon that occurs in the porous electrodes.

The patterned electrodes have a well-defined 2D structure, and the TPB length can be accurately defined from the geometrical interface between the three phases.⁶ The cermet electrodes, on the other hand, have a complex 3D microporous structure, and their TPB length is designated per unit volume of the electrode (m/m³), hence the term TPB density. Three distinguished terms associated with the TPB density of a cermet electrode have been used in this text or in relevant literature including 1) percolated TPB density, 2) total TPB density, and 3) effective TPB density. The "percolated TPB density" refers to the TPBs formed by percolated phases (ionic phase, electronic phase, and gas phase/pores) that extend throughout the entire thickness of the composite electrode. It defines the upper

limit of the electrochemically active reaction sites and therefore the "active TPB density" term has also been used in literature to identify the same.^{7–9} The "total TPB density" includes both percolated and nonpercolated TPB densities. Several experimental and theoretical approaches have been developed to determine the microstructural details of the cermet electrodes including TPB densities such as X-ray computed tomography,¹⁰ focused ion beam scanning electron microscopy (FIB-SEM),^{11,12} and 3D microstructure model.¹³ The percolated TPB density of Ni-YSZ anodes, determined with the help of these techniques, is typically 10^{12} – 10^{13} (m/m³). However, a recent simulation study using TPB-based kinetics derived from the patterned electrode cells has concluded that only a fraction of the percolated TPB density is required or available during fuel cell operation to carry out the electrochemical reactions and generate the desired cell current density.¹⁴ This fraction of the percolated TPB density that effectively contributes to the current production during cell operation is termed as "effective TPB density." Since the study employed the experimental data of a thick anode-supported button cell for model validation and findings regarding the effective TPB density, further investigations using thin anode layers were suggested.

Besides TPB density, anode thickness is another crucial parameter in the design and performance of a SOFC. The state-of-the-art anode-supported SOFCs have a dedicated anode functional layer (AFL) adjacent to the electrolyte, with a thickness of few micrometers, and a relatively thick anode support layer, typically higher than 300 µm. The microporous anode structure is responsible for mass transport to and from the anode/electrolyte interface, besides electrocatalytic activity, so the thickness beyond electrocatalytically active layer directly contributes to the reduction in the cell performance. Unlike cells supported by electrolytes, anode-supported cells feature a thin layer of electrolyte. This significantly reduces the ohmic loss caused by the thickness of the electrolyte. As a result, these cells may operate at lower temperatures and exhibit superior performance, provided that activation and concentration losses are managed. The metal-supported cells have recently gained considerable attention in SOFC development because they have relatively thin electrode and electrolyte layers and offer several advantages over anode-supported or electrolytesupported SOFCs.¹⁵ These advantages include increased mechanical strength, excellent thermal and redox cycling tolerance, inexpensive materials, and rapid start-up capability.

Studies have found that the electrochemical reactions in the cermet anode are contained in a thin anode layer adjacent to the anode/electrolyte interface. The thickness of the layer is commonly regarded as the electrochemically active or active anode thickness.¹⁶ As summarised previously,¹⁷ the active anode thickness is typically in the range of $2-40 \,\mu\text{m}$, depending upon the cell design and operational conditions. Although active thickness plays a significant role in electrode design, it does not offer a definitive basis for comparing the performance of diverse electrode designs that operate in varying conditions. Moreover, relying solely on active thickness is inadequate when simulating TPB-related processes, including cell degradation caused by anode poisoning and thermal/redox cycling. For instance, during sulfur poisoning, sulfur diffuses into the nickel bulk, detacing nickel particles from their original positions and causing an irreversible reduction in the TPB length.^{18–20} A comparable phenomenon occurs when nickel particles agglomerate due to thermal or redox cycling, resulting in a notable decrease in the TPB length and an elevation in the electrode polarization resistance.²¹ Therefore, an optimum anode thickness and information on the effective TPB density are imperative for better cell design and operation. To the author's knowledge, very limited information is available on the effective TPB density and no study is available to discuss the relationship between effective TPB density and active anode thickness. However, previous studies indicated the order of effective TPB density.^{14,17} Therefore, there is a need to investigate this relationship, motivating the current study to facilitate the design and fabrication of anode or at least in fuel cell modeling.

The performance of SOFC electrodes is experimentally determined by either polarization measurement or electrochemical impedance spectroscopy (EIS). Both numerical²² and empirical/analytical⁹ models have been developed for performance evaluation in simulation studies. Commonly employed analytical models include the nonlinear Butler-Volmer (BV) equation,⁹ linearly approximated BV equation,²³ and BV formalism.²⁴ There has been much discussion on using the BV equation to describe electrode kinetics in various fields of electrochemistry.²⁵ This study uses BV formalism proposed by Zhu et al.²⁴ and the TPB-based kinetics determined from previously reported patterned anode cells.¹⁴ Since the formalism is analytically derived from the detailed reaction scheme of electrochemical hydrogen oxidation, it considers the effect of concentrations on the exchange current density, closely matches the reaction orders with the experimentally determined values, and guarantees the thermodynamic consistency in the resulting expression. The experimental current-voltage (I-V) curves for the varying anode are obtained from the literature and used here for model validation and determination of the relationship between active anode thickness and the effective TPB density.

2 | MODEL DEVELOPMENT

2.1 | Model geometry

Four different experimental data sets, reported previously,^{26–29} were used in this study for model validation. The experimental results of these studies include I-Vcurves of Ni-YSZ anode-supported SOFCs fed with humidified hydrogen fuel at their respective reported temperatures ranging from 700°C to 800°C. Further, these studies used varying dimensions of the membraneelectrode assembly (MEA), particularly the thickness of the anode substrate and the AFL. The actual geometrical and elementary parameters of the cells are given in Table 1. A representative sketch of the 2D axisymmetric model used for the simulations is shown in Figure 1A, and an extended view of the complete button cell along with flow channels is shown in Figure 1B. The cell and channel dimensions in the model view are arbitrary and may vary depending on the actual dimensions used in the experimental study. The fuel is transported to the anode via the inner cylindrical pipe, while the space between the inner and outer cylinders is used for dispensing the products. The cathode is exposed to either the surrounding ambient air or oxygen, as mentioned in the experimental study.

2.2 | Mathematical model

Using the available physics modules in the COMSOL Multiphysics software, a 2D axisymmetric model is created and implemented. The model development is based on the following assumptions:

- All gases follow ideal behavior.
- The system operates under steady-state conditions, with a uniform temperature distribution in the cell cross-section.
- The fuel oxidation occurs via the hydrogen spillover mechanism.
- The microstructure is uniform within each layer of the electrodes.

The secondary current distribution interface is used to specify the transport of charged ions in the electrolyte and the flow of electric current in the porous electrodes. This interface combines Ohm's law and charge balance principles. The electrode kinetics for the charge transfer

used in the simulation. ^{26–29}	
arameters of the cells	
Geometrical and elementary p	
TABLE 1	

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Parameter	Cell AFL-0	Cell AFL-3.9	Cell AFL-7.6	Cell AFL-10.1	Cell AFL-20	Cell AFL-40	Cell AFL-60	Cell AFL-0	Cell AFL-5	Cell AFL-10	Cell AFL-15	Cell AFL-40	Cell AFL-60	Cell AFL-80	Cell AFL-120	
Anode																
Diameter (µm)	15	15	15	15	18	18	18	13	13	13	13	20	20	20	20	
Substrate thickness (µm)	560	560	560	560	006	006	006	600	600	600	600	600	600	600	600	
AFL thickness (µm)	0	3.9	7.6	10.1	20	40	60	0	5	10	15	40	60	80	120	
Porosity (–)	0.659	0.657	0.653	0.652	0.698	0.676	0.648	0.55	0.55	0.55	0.55	0.25	0.25	0.25	0.25	
Porosity/tortuosity ratio (–)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.15	0.1	0.07	0.05	0.05	0.05	0.05	
Conductivity (S/cm)	305.7	305.7	305.7	307.5	308.1	308.1	308.1	309.5	309.5	309.5	309.5	309.5	309.5	309.5	309.5	
Electrolyte																
Diameter (µm)	15	15	15	15	18	18	18	13	13	13	13	20	20	20	20	
Thickness (µm)	4	4	4	4	12	12	12	8	∞	8	8	30	30	30	30	
Conductivity (S/m)	0.22	0.27	0.33	0.25	0.9	0.7	0.6	3.65	4	2.1	2	2	1.2	1.2	0.8	
Cathode																
Diameter (µm)	15	15	15	15	18	18	18	13	13	13	13	20	20	20	20	
Thickness (µm)	10	10	10	10	15	15	15	20	20	20	20	20	20	20	20	
Porosity (–)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	
Porosity/Tortuosity ratio (–)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
Conductivity (S/cm)	125.7	125.7	125.7	127.5	127	127	127	127.9	127.9	127.9	127.9	127.9	127.9	127.9	127.9	
General parameters																
Temperature (°C)	700	700	700	700	750	750	750	800	800	800	800	800	800	800	800	
Pressure (atm)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
OCV (V)	1.03	1.06	1.06	1.05	1.018	1.026	1.038	1.08	1.12	1.14	1.0841	1.015	1.031	0.962	1.024	SHA
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FIGURE 1 Sketch of button cell and test assembly used for the simulation. AFL, anode functional layer; YSZ, yttria-stabilized zirconia. (A) 2D axisymmetric model; (B) expanded view of the complete button cell model.



TABLE 2 Conservation equations used in the model.

Category	Domain	Equation
Mass conservation	Inside gas channels	$ abla \cdot (ho \boldsymbol{u}) = 0$
	Inside electrodes	$ abla \cdot (ho \boldsymbol{u}) = \dot{W}$
	Inside anode	$\dot{W}=\left(M_{ m H_2O}-M_{ m H_2} ight)rac{S_{ m an}i_{ m an}}{2F}$
	Inside cathode	$\dot{W} = M_{O_2} \frac{S_{Ca} i_{ca}}{4F}$
Species conservation	Inside electrodes	$\nabla \cdot (\rho \omega_i \boldsymbol{u}) = -\nabla \cdot \mathbf{J}_i + \dot{R}_i$
	Inside anode	$\dot{R}_{H_2} = -\frac{M_{H_2}S_{an}i_{an}}{2F}, \dot{R}_{H_2O} = \frac{M_{H_2O}S_{an}i_{an}}{2F}$
	Inside cathode	$\dot{R}_{\rm O_2} = -\frac{M_{\rm O_2}S_{ca}i_{ca}}{4F}$
Charge conservation	Inside electrodes	∇ . $i_{elec} = \nabla$. $\left(-\sigma_{elec}^{eff} \nabla \phi_{elec} \right) = \dot{Q}_{elec}$
	Inside electrodes	$\nabla. \ i_{ion} = \nabla. \left(-\sigma_{ion}^{eff} \nabla \phi_{ion} \right) = -\dot{Q}_{ion}$
	Inside electrolyte	$ abla. i_{ion} = abla. \left(-\sigma_{ion}^{e\!f\!f} abla \phi_{ion} \right) = 0$
Momentum conservation	Inside gas channels	$\rho(\boldsymbol{u}\cdot\nabla)\boldsymbol{u} = -\nabla\cdot(P\boldsymbol{I}) + \nabla\cdot\left[\mu(\nabla\boldsymbol{u} + (\nabla\boldsymbol{u})^T) - \frac{2}{3}\mu(\nabla\cdot\boldsymbol{u})\boldsymbol{I}\right]$
	Inside electrodes	$\left(\frac{\mu}{\kappa} + Q_{mass}\right)\boldsymbol{u} = -\nabla \cdot (P\boldsymbol{I}) + \nabla \cdot \left[\frac{\mu}{\varepsilon}(\nabla \boldsymbol{u} + (\nabla \boldsymbol{u})^T) - \frac{2}{3}\frac{\mu}{\varepsilon}(\nabla \cdot \boldsymbol{u})\boldsymbol{I}\right]$

reactions are defined by the Butler–Volmer formalisms derived by Zhu et al.,³⁰ in combination with the TPBbased kinetics derived previously¹⁴ using patterned electrode cells. The transport of concentrated species interface is used to define the transport of the gas-phase reactants and products through gas channels and porous electrodes. The Maxwell–Stefan model is widely used to define multicomponent diffusion. To account for the species collisions with walls in the porous electrodes, the binary diffusivities are empirically corrected by incorporating the Knudsen diffusion and porous media flow interface is employed to calculate the velocity and pressure fields. This interface enables smooth transitions between flow in the porous media, which is determined by the Brinkman equations, and gas flow in the channels, which is characterized by the Navier–Stokes equations. Due to the assumption of the isothermal conditions, heat transfer physics is not used for this model. The conservation equations used for each physics interface are summarised in Table 2, and other constitutive equations used in the computation or postprocessing of the results are summarized in Table 3. The boundary conditions are summarized in



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Property	Constitutive equation
Butler-Volmer formalism of hydrogen oxidation reaction	$i_{an} = i_{an}^{o} \left[\exp\left(\frac{(1+\beta_{a})F\eta_{act,an}}{RT}\right) - \exp\left(-\frac{\beta_{c}F\eta_{act,an}}{RT}\right) \right]$
Butler–Volmer formalism of oxygen reduction reaction	$i_{ca} = i_{ca}^{o} \left[\exp\left(\frac{\beta_{a}F\eta_{act,ca}}{RT}\right) - \exp\left(-\frac{\beta_{c}F\eta_{act,ca}}{RT}\right) \right]$
Anode exchange current density	$i_{an}^{o} = 2l_{TPB}Fk_{3r}(K_{2}K_{3})^{\frac{\beta_{3c}}{2}}(K_{5})^{1-\frac{\beta_{3c}}{2}} \left[\frac{(K_{1}p_{H_{2}})^{\frac{\beta_{3c}}{2}}(p_{H_{2}O}/K_{4})^{1-\frac{\beta_{3c}}{2}}}{1+(K_{1}p_{H_{2}})^{\frac{1}{2}}}\right]$
Cathode exchange current density	$i_{ca}^{o} = i_{O_2}^{*} \left[\frac{\left(p_{O_2} / p_{O_2}^{*} \right)^{\frac{1}{4}}}{1 + \left(p_{O_2} / p_{O_2}^{*} \right)^{\frac{1}{2}}} \right]$
Effective electronic conductivity	$\sigma_{elec}^{eff} = \sigma_{elec} \theta_{E.C.} (1 - \varepsilon)$ (For porous electrodes)
Effective ionic conductivity	$\sigma_{ion}^{eff} = \sigma_{ion}(1 - \theta_{E.C.}) (1 - \varepsilon) \text{ (For porous electrodes)}$ $\sigma_{ion}^{eff} = \sigma_{ion} \text{ (For electrolytes)}$
Equilibrium cell voltage	$E_{rev} = -\frac{\Delta G_{\rm H_2-H_2O}^0}{2F} + \frac{RT}{2F} \ln\left(\frac{a_{\rm H_2}a_{\rm O_2}}{a_{\rm H_2O}}\right)$
Cell voltage	$V_{cell} = E_{rev} - \eta_{conc,an} - \eta_{conc,ca} - \eta_{act,an} - \eta_{act,ca} - \eta_{ohm}$
Concentration overpotential	$\begin{split} \eta_{conc,an} &= \frac{_{RT}}{_{2F}} \ln \left(\frac{p_{\rm H_2}^b}{p_{\rm H_2}^{_{TTB}}} \cdot \frac{p_{\rm H_2O}^{_{TPB}}}{p_{\rm H_2O}^b} \right) \text{(For anode)} \\ \eta_{conc,ca} &= \frac{_{RT}}{_{4F}} \ln \left(\frac{p_{O_2}^b}{p_{CD}^{_{TPB}}} \right) \text{(For cathode)} \end{split}$
Activation overpotential	$\eta_{act,an} = \Delta E_{an/elec} - \Delta E_{an/elec}{}^{eq} \text{ (For anode)}$ $\eta_{act,ca} = \Delta E_{ca/elec} - \Delta E_{ca/elec}{}^{eq} \text{ (For cathode)}$
Ohmic overpotential	$\eta_{ohm} = iR_{tot}$
Flux of specie " <i>i</i> " in the electrodes	$J_{i} = -\rho\omega_{i}\sum_{k} D_{ik.eff}\left(\frac{M}{M_{k}}\left(\nabla\omega_{k} + \omega_{k}\frac{\nabla M}{M}\right) + (x_{k} - \omega_{k})\frac{\nabla P}{P}\right)$
Effective binary diffusivity	$D_{ij,eff} = \frac{\varepsilon}{2\tau} \left(\frac{1}{\frac{1}{D_{ij}} + \frac{1}{D_{ik}}} + \frac{1}{\frac{1}{D_{ij}} + \frac{1}{D_{jk}}} \right)$
Binary diffusion coefficient	$D_{ij} = \frac{10^{-3}T^{1.75} \left(\frac{1}{M_i} + \frac{1}{M_j}\right)^{0.5}}{P\left[\left(\Sigma V_i\right)^{\frac{1}{3}} + \left(\Sigma V_j\right)^{\frac{1}{3}}\right]^2}$
Knudsen diffusion coefficient	$D_{\left(rac{i}{j} ight)k}=rac{2r_{p}}{3}\sqrt{rac{8RT}{\pi M_{rac{i}{j}}}}$

Table 4. The labels of boundary conditions have been elaborated on previously.¹⁷

2.3 Solution methodology

The commercial finite element software COMSOL Multiphysics V5.1 was used to implement the mathematical model. The equations for charge, mass, and momentum transport are simultaneously solved using the default MUMPS solver with a relative tolerance of 10⁻⁴. Gas channels and anode substrate were discretized with unstructured triangular mesh elements, whereas the AFL, electrolyte, and cathode were discretized with structured quadrilateral elements. To ensure the accuracy and reliability of the results, the grid in the computational domain was refined, and grid independence was ensured. The refined grid enabled the model to produce consistent results to draw meaningful conclusions.

TABLE 3 Constitutive equations

used in the model.

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TABLE 4 Boundary conditions.

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Category	Anode/channel interface	Anode/electrolyte interface	Cathode/electrolyte interface	Cathode/channel interface
Ionic charge conservation	Insulation	Continuity	Continuity	Insulation
Electronic charge conservation	Grounded	Insulation	Insulation	Cell potential
Mass conservation	Continuity	Insulation	Insulation	Continuity
Momentum conservation	Continuity	Wall	Wall	Continuity

3 | **RESULTS AND DISCUSSIONS**

3.1 | Model validation and polarization behavior

First, the mathematical models and inputs are evaluated for accuracy by comparing simulation and experimental results. The geometrical and elementary parameters used in the simulation are shown in Table 1. The open circuit voltage, reported in the corresponding experimental studies, was used instead of calculating from the Nernst equation to avoid experimental and simulation inconsistencies. The TPB density, used in the exchange-current density relationship, was the only free-fit parameter in the simulation. The TPB density was adjusted to match the simulated and experimental I-V relationship. The cell voltage was linearly varied from the OCV to 0.25 V to draw the current-voltage curve, study the electrochemical behavior of the cell, and obtain vital information about the distribution of gas concentration, local current density, and cell potential, velocity, and pressure. The experimental and simulated I-V curves of all 15 cells from four different data sets, mentioned in Section 2.1, are shown in Figure 2.

The actual and simulated curves show a qualitative agreement at the set TPB density values, which validates both the model and the input parameters utilized in the simulation. At least a variation of three orders of magnitude in the best-fit value of the TPB densities has been observed for different cells studied in this work. That is, the highest value is observed for Chen et al.²⁶ Cell AFL-10.1 ($6.9 \times 10^8 \text{ m/m}^3$), while the lowest value is observed for Kong et al.²⁹ Cell AFL-60 $(2.5 \times 10^5 \text{ m/m}^3)$. Previously, Tabish et al.¹⁴ reported the effective TPB density of $1.78 \times 10^7 \text{ m/m}^3$ for a thick anode-supported button cell, 1.2 mm thick anode, which is well within the range found in this work. As far as the authors are aware, there are no other studies available for comparison of the density values of the TPB. Nonetheless, the considerable variation can be attributed to the synergic effect of various factors, such as the microstructure and porosity of the electrode, the operating conditions, the material composition used, and the fabrication techniques employed.

3.2 | Assessment of the active anode thickness

Active anode thickness refers to the region of the anode layer near the anode/electrolyte interface where approximately 90% of electrochemical reactions occur.¹¹ This region is crucial for efficient fuel cell operation, provided that the anode is adequately thick to facilitate these reactions. To determine the active anode thickness, the current density distribution is analyzed across the anode thickness. A representative distribution of the current density for Chen et al.²⁶ Cell AFL-10.1 at different cell voltages is shown in Figure 3A. The current density is highest at the interface between the anode and electrolyte, gradually decreasing exponentially as one moves away from the interface. Likewise, the total interfacial current density increases as the cell voltage decreases. There is no external current flow when the cell operates at OCV point, and the electrode reactions occur at a relatively low rate. The current density is therefore equivalent to the exchange current density. As the cell is discharged and the voltage drops, the electrode potential becomes more negative, increasing the electrochemical reaction's driving force. As a result, the electrochemical activity near the anode/electrolyte interface increases, and the interfacial current density increases, leading to a higher electron transfer rate at the electrode/electrolyte interface.

The effect of overpotential on the active anode thickness is shown in Figure 3B. As can be observed, the larger values of over-potential lead to a thinner active anode layer. This also aligns with the reported trend.^{11,32–34} This observation implies that with an increased active anode thickness, the anode benefits from more reaction sites, resulting in a reduced overpotential. Besides overpotential, the active anode



FIGURE 2 Experimental and simulated current–voltage (*I–V*) curves. The experimental data refer to the studies of (A) Chen et al.²⁶; (B) Lin et al.²⁷; (C) Chen et al.,²⁸ and (D) Kong et al.²⁹ The solid lines indicate corresponding simulated curves. Details of the input parameters are provided in Table 1. AFL, anode functional layer.



FIGURE 3 Assessment of the active anode thickness based on Chen et al.²⁶ Cell AFL-10.1, (A) distribution of current density in the anode layer and (B) the effect of total overpotential on the active anode thickness. The "0" value at the *x*-axis represents the anode/electrolyte interface.

thickness is considerably affected by reaction kinetics and the effective conductivity of the anode, which depend on microstructural properties, the temperature and moisture content of the fuel. Therefore, the active anode thickness of all 15 cells is evaluated and compared at a common overpotential of 0.4 V.

3.3 | Relationship between effective TPB density and active anode thickness

Figure 4 presents the active anode thickness and effective TPB density values found in this study. The active anode thickness of the data sets of Chen et al.,²⁶ Lin et al.,²⁷ and



FIGURE 4 Relationship between effective triple-phase boundary density and active anode thickness.

Chen et al.²⁸ is in the range of $4.41-12.14 \,\mu\text{m}$. These cells are referred to as high-performing cells. However, the datasets of Kong et al.²⁹ yield an active thickness above 100 μ m and labeled as low performing cells. It is pertinent to mention that the exchange-current density of datasets of Kong et al.²⁹ is also almost three orders of magnitude lower than the high-performing cells. The categorization of cells as either high- or low-performing is merely based on their power density values and the thickness of their active anode.

The performance of SOFCs is directly influenced by the thickness of the active anode layer, which is closely associated with the AFL in the literature. For instance, Chen et al.²⁶ reported that an optimal thickness of 7.6 μ m for the AFL significantly improves the cell's performance, resulting in a peak power density of 0.906 W/cm². Chen et al.²⁸ found that the gas impermeability generally improves as the AFL thickness increases, albeit the ohmic resistance increases. The cell with a 5-µm-thick AFL showed excellent performance with an output power of 2.63 W/cm² at 800°C. Moon et al.³⁵ reported that as the AFL thickness increases, the cell performances generally improve because of the number of active sites. Similarly, Bi et al.³⁶ reported that the incorporation of the AFL leads to a reduction in both contact resistance and polarization resistance for the cell. As summarized previously,¹⁷ the active anode thickness is typically in the range of 2-40 µm depending upon the cell design and operating conditions through higher active thickness has also been reported.

The literature commonly reports the TPB density that percolates throughout the electrode, previously referred to as active TPB density.⁸ Our previous studies employing TPB-based kinetics concluded that only a minor fraction

of the percolated TPB density is sufficient or effectively available to fulfill the electrochemical requirements of the cell. In contrast, the major fraction stays idle during the cell operation.^{14,17} To the author's knowledge, no study has considered a similar approach to determine the effective TPB density values. The relevant simulation studies consider percolated TPB density for estimating specific catalyst area and use empirically determined exchange current density to simulate the experimental data.³⁷ The specific catalyst area is an essential parameter in electrode electrochemistry and incorporates surface reactions such as adsorption/desorption of reactants/ products and surface diffusion. It is also required to translate the current produced per unit TPB length to the exchange-current density.¹⁴ The specific catalyst area ranges from 1×10^5 to 2.2×10^6 m²/m³.³⁸ For optimal cell design, it is superior to consider both the effective TPB density, determined through the TPB-based kinetics, instead of percolated TPB density and the active anode thickness, as they respectively impact the microstructural activity and anode thickness. This approach is especially favorable for accurately simulating the cell performance during prolonged operation and for fuel components that can potentially pollute the TPB sites.

An inverse relationship between the effective TPB density ($\lambda_{TPB}^{\text{effective}}$) and active anode thickness (t_a^{active}) is evident from Figure 4 and can be visualized as a linear line on a log–log scale. It can be observed that the linear line on the log–log scale reasonably fits the simulated data where the slope of this line is -2.56 ± 0.06 , which signifies the strength of the relationship between the two parameters. The empirical relationship, therefore, can be written as

$$\log \left(\lambda_{\text{TPB}}^{\text{effective}} [\text{m}/\text{m}^3] \right) = -2.56 \log \left(t_a^{\text{active}} [\mu\text{m}] \right) + 10.67.$$

The relationship reveals that the lower the active anode thickness is, that is generally the case of highperforming cells or higher overpotential for a given cell operation, the higher the effective TPB density will be. That is quite intuitive and suggests that the effective TPB density approaches the percolated TPB density at a very high current density. This also implies that, likewise, active anode thickness, the effective TPB density is also a function of the operational conditions. Despite the fact that active anode thickness varies with cell operation level, TPB density is commonly used in SOFC simulation studies as a fixed parameter corresponding to phase perculation. The above empirical relationship also suggests that the highest value of the effective TPB density is 10^{10.67} that is at least one order of the 3892

magnitude lower than the commonly reported value of the percolated TPB density. It can also be anticipated that a major fraction of the percolated TPB density remains idle during the cell operation.

4 | CONCLUSION

This study thoroughly investigates the effective TPB density in SOFCs and its relationship with a better-known parameter active anode thickness. The experimental current-voltage behavior of four different data sets employing different cell geometry and operating conditions were obtained from the published literature. A steady state and isothermal model was developed to simulate the experimental data using previously developed TPB-based kinetics. The qualitative agreement between the experimental and simulated current-voltage curves confirmed the validity of the model and input parameters used. The TPB density was adjusted to match the simulated and experimental results, highlighting its significance as a key parameter in SOFC performance.

The electrochemical reactions that take place near the anode/electrolyte interface were found to be closely associated with the active anode thickness, as revealed by the analysis. The thickness of the active anode layer was found to affect the distribution of charge-transfer current density across the anode, with a higher density observed near the interface. Furthermore, the study explored the relationship between active anode thickness and effective TPB density. An inverse relationship has been observed between the two parameters. As the active anode thickness decreases, the effective TPB density tends to increase so much that the effective TPB density approaches the percolated TPB density at high current densities. It indicated that a significant fraction of the TPB sites remained idle during cell operation, emphasizing the importance of optimizing TPB utilization for improved cell performance.

The findings of this study have significant implications for the design and operation of SOFCs. By considering both active anode thickness and effective TPB density, it is possible to help better understand the microstructural activity, design better cells, and estimate the electrochemical performance of the cells for long-term operations. Furthermore, the findings of this study can guide the development of more efficient and reliable SOFCs by optimizing the utilization of TPB sites.

NOMENCLATURE

- c_k concentration of specie $k \pmod{m^3}$
- E_{ct}^{act} activation energy of the charge-transfer reaction (J/mol)

- E_{cell} cell voltage (V)
- *i/i*⁰ current density/exchange current density (A/m²) *I* identity matrix
- J_i Mass transfer flux (kg/m² s)
- k_3^{o} Arrhenius pre-exponent of charge transfer reaction (mol/cm s)
- k_{3r} backward rate constant of the charge transfer reaction^{14,24}
- K_1 - K_5 equilibrium constants of elementary reactions^{14,24}
- l_{tpb}/l_{tpb}^{ν} area-specific TPB length (m/m²)/TPB density (m/m³)
- *p*/*P* partial pressure/pressure (atm)
- \dot{Q} charge-transfer rate (a/m³)

 \dot{W}/\dot{R} total/component mass source term (kg/m³ s)

- s volume-specific surface area of the electrode (m^2/m^3)
- *u* velocity vector (m/s)

GREEK LETTERS

- α charge transfer coefficient
- ε porosity
- β symmetry parameter
- η overpotential
- κ permeability (m²)
- ρ density of the fluid (kg/m³)
- μ dynamic viscosity of the fluid (Pa s)
- σ ionic/electronic conductivity (1/ Ω m)
- ω mass fraction (kg/kg)
- au tortuosity
- ϕ charge potential (V)

SUBSCRIPTS/SUPERSCRIPTS

act	activation
an/ca	anode/cathode
conc	concentration
eq	equilibrium
ion/elec	ionic/electronic
ohm	ohmic
TPB/tpb	triple-phase boundary

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