



## Analytical solutions for extended surface electrochemical fin models



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### HIGHLIGHTS

- Exact solutions were obtained to simulate current passages in SOFC electrodes.
- A solid oxide fuel cell (SOFC) electrode was selected as a test case for these studies.
- Assess geometry influence 3-D electrode microstructure on performance.
- Performance was correlated to geometrical changes in the electrode.

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### ABSTRACT

Exact solutions were obtained for variations in the potential and the current for three axisymmetric geometries, with positive, negative and zero curvatures, which simulate current transport in fuel cell electrodes. These solutions can be used to assess the influence of geometry on performance for three dimensional electrode microstructures. A solid oxide fuel cell (SOFC) electrode was selected as a test case for these studies. From the exact solutions, simulations of current flow and potential drop for one dimensional networks in SOFC electrodes were performed. Numerical tests demonstrated that surfaces with positive curvature have greater current flow for the same potential drop due to higher current losses through the lateral surface area. The study also showed that zero curvature solutions will be sufficiently accurate for positive or negative curvature geometries for moderate radius changes, but differ significantly from positive or negative curvature solutions for more extreme radius changes. Analytical solutions indicate fundamental differences in geometry and its influence on current flow. Based on the results of the simulations, an approximate solution, based on one non-dimensional parameter, was developed for estimating the effects of extreme changes in cross-section area.

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### 1. Introduction

The composite electrodes applied in electrochemical energy storage and conversion devices are heterogeneous functional material systems that must support the effective movement of charge generated by the electrochemical interaction between electrode phases. Such electrodes may include ceramic–metal (cermet) composites and mixed conducting electrodes found in solid oxide fuel cells (SOFCs) [1], carbon and transition metal oxide electrodes of Li-ion batteries [2,3], and porous titania films used in dye-sensitized solar cells [4,5]. These chemically active

composite systems require the presence of sites that support fundamental chemistry and sufficient transport networks that deliver reactant species to and byproducts from these active sites. Considering these two key requirements, the deliberate design of microstructural geometry in composite electrodes can benefit performance by increasing the efficacy of active sites and by promoting the efficient movement of charge through conductive phases to the active surfaces.

Within SOFC electrodes, the effective transport of ions and electrons to active sites is of particular interest. In more common cermet electrodes, these sites reside where the solid ion and electron conducting phases meet an open pore phase that enables transport of gaseous reactants. In electrodes that support the mixed conduction of ionic and electronic charge carriers these reaction sites may be distributed over a broader portion of the solid–pore interface. It has generally been found that the extension of active

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**Nomenclature**

$a$	radius of cross-section, m	$P_\nu$	Legendre function of order $\nu$
$A_1, A_2$	arbitrary constants	$R$	charge transfer resistance, $\Omega \text{ m}^2$
$A_c$	area of cross-section, $\text{m}^2$	$R'_c$	equivalent cross-section resistance, $\Omega$
$A_{\text{eff}}$	effective area of cross-section, $\text{m}^2$	$R_s$	equivalent surface resistance, $\Omega$
$A_s$	surface area, $\text{m}^2$	$r_o, r_e$	entry and exit radii respectively, m
$i_c$	total current through cross-section, A	$x$	transformed axial coordinate $k(z - z_0)$
$I_1, K_1$	modified Bessel functions of order one	$z$	axial coordinate, m
$k$	curvature or slope, $\text{m}^{-1}$	$z_0$	axial offset, m
$L$	segment length, m	$\alpha$	hyperbolic roots, $\pm\sqrt{1 + 2/\sigma Rk}$
$\ell$	symmetric half segment, length, m	$\beta$	equivalent circuit coefficient
		$\Phi$	transformed potential, $\varphi/a$
		$\varphi$	potential, V

sites away from the planar interface between electrode and electrolyte layers of the cell can reduce overall polarization resistance within the electrode and increase SOFC performance. This extension is often achieved through the fabrication of a functional layer near the electrode/electrolyte interface with a finer microstructure than the porous electrode support. This extended active surface results in the more effective transfer of ionic charge carriers from the bulk electrolyte to active sites within the composite electrode [6,7].

The coupled electrochemistry and charge transport that occurs in these electrodes have been explored using a variety of techniques including thin-film electrode models [6,8], extended surface electrode models [7,9], and percolation theory [10–14]. A commonality in these modeling approaches is the application of a second order, ordinary differential equation comparable to the equation describing heat transfer from a thermal fin. Early application of this equation can be attributed to Kenjo et al. [6,8], who used a thin-film model to predict the polarization resistance of SOFC electrodes with varying composition and microstructural quality. This approach abstracted the dispersed ionic conducting phase as a thin film coating the electronic conducting phase and addressed both charge transport and microstructural geometry through the use of a single lumped parameter. It was found that materials that sintered well, forming wide contact areas between individual particles in the composite electrode, displayed superior performance compared to materials with poor sinterability. It was also demonstrated that for well sintered electrodes polarization resistance could be reduced by increasing the thickness of the active electrode. However, this improvement showed a diminishing return that suggests a trade-off between transport losses. The thin-film model of Kenjo et al. was adapted to an extended surface formalism by Tanner et al. [7], who treated the ionic conducting phase as a set of rectangular corrugations, coated with electrocatalyst, extending from the bulk electrolyte. This approach added microstructural detail by moving away from the lumped parameter description of charge transport and microstructure. Instead, microstructure was accounted for through the sizing and separation of the extended ion conducting surfaces. Other descriptions of charge transport within composite SOFC electrodes have drawn on percolation theory to define effective conductivity and other charge transfer parameters [10–14]. As in the analytical approaches provided by Kenjo et al. and Tanner et al., these approaches apply a governing equation comparable to that of a constant cross-section thermal fin.

The effects of varying particle contact geometry have been investigated by Zhao and Virkar [15] through the development of analytical expressions for the effective conductivity of sintered electrodes. The incorporation of more detailed microstructural geometry within extended surface electrode models was also

explored by Nelson et al. [9] through the use of a governing equation that accounts for variable cross-section geometry in the extended surface. In this analysis, chains of ionic conducting particles extending from the electrolyte were simulated based on an iterated series of truncated cones. As illustrated in Fig. 1, these particle chains can be considered to comprise the active layer of the electrode that resides near the electrode–electrolyte interface. In electrodes with good connectivity such chains may extend into the porous electrode support. The variable cross-section extended surface approach was found to be capable of replicating experimentally observed polarization resistances in SOFC electrodes, inclusive of resistive effects linked to reduced interparticle contact areas that result when electrode particles are not sufficiently sintered [9]. Further investigation of the impacts of multi-dimensional transport and space charge regions at contact points between particles demonstrated that the analytical extended surface models provided an accurate assessment of electrode performance, particularly for purposes of screening potential microstructural designs [16]. Thus it has been found that variable cross-section extended surface models present a promising tool for the more deterministic design of electrode microstructures. However, the development of a more robust means of assessing electrode quality can benefit from extension of the electrochemical fin modeling concept to a more diverse set of particle shapes that may be present in electrode microstructures. For example, the fabrication of electrodes based on spherical particles has been demonstrated using samaria-doped ceria, and the conductivity of these porous composites has shown clear sensitivity to microstructural geometry [15].

In the present work exact analytical solutions are presented for a variety of particle shapes that may be used to simulate an extended surface electrode. These shapes include conical particles similar to those investigated previously [9,16], as well as particles with spherical shapes and particles with a profile based on a hyperbolic cosine function. These latter two particle profiles are illustrated in Fig. 1b. Using a set of basic parametric studies, transport effects associated with particle curvature, variable cross-sectional area, surface area, and length are investigated to further elucidate the role of microstructural geometry in electrode performance. The effects of material properties and boundary conditions are included in the solutions and can also be addressed to better determine the interaction between particle shape and the physical phenomena that govern electrode operation. For example, the effects of curvature on surface current losses can be examined since exact solutions for positive (spherical surface), zero (conical surface) and negative (hyperbolic surface) curvatures have been developed. Hence, even small differences in current loss can be used to find trends. The analytical solutions have shown conclusively that positive

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