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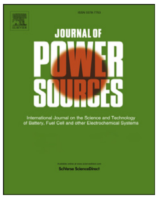

A calibrated hydrogen-peroxide direct-borohydride fuel cell model

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HIGHLIGHTS

- A numerical model is developed for a H_2O_2-direct borohydride fuel cell (H_2O_2-DBFC).
- Global reactions in the model are calibrated vs. a simple experimental H_2O_2-DBFC.
- The calibrated model is used to predict the losses from parasitic side reactions.
- Maximum power density and system efficiency coincide due to parasitic side reactions.
- H^+ reduction contributes to cathode current density when H_2O_2 is transport limited.

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ABSTRACT

A numerical model with global reaction rates is calibrated to measurements from a simple hydrogen-peroxide direct-borohydride fuel cell (H_2O_2-DBFC), and then used to unravel complex electrochemical and competing parasitic reactions. In this H_2O_2-DBFC, fuel (1–50 mM $NaBH_4$/2 M NaOH) is oxidized at a Au anode and oxidizer (10–40 mM H_2O_2/1 M H_2SO_4) is reduced at a Pd:Ir cathode. Polarization curves and electrode potentials, as functions of fuel and oxidizer feeds support global reaction rate parameter fitting. The measurements and calibrated model showed H_2O_2 decomposition at the cathode depresses open circuit voltage from 3.01 V theoretical to 1.65 V, and when H_2O_2 supply is limited, cathode potentials are sufficiently negative to make H^+ reduction to H_2 thermodynamically favorable. Calibrated model results show that thin concentration boundary layers limit reactant utilization and current density. Decreasing the inlet concentrations, flow rates, and cell voltage slow parasitic reactions and favor desirable charge transfer reactions. Peak conversion efficiency and peak power density coincide because thermodynamic efficiency and parasitic reaction rates decrease (relative to charge transfer reaction rates) with increasing current density. We conclude that the performance of a fuel cell with parasitic side reactions can be predicted through numerical modeling.

1. Introduction

Direct borohydride fuel cells (DBFCs) have been considered for applications ranging from portable consumer electronics to vehicle propulsion. The term DBFC refers to diverse fuel cell configurations in which BH_4^- is oxidized at the anode; review papers [1–8] summarize the variety of DBFC chemistries, catalysts and topologies explored to date. Two major classes include those utilizing acidic or alkaline oxidizer solutions. The DBFC studied herein uses $NaBH_4$/NaOH fuel and H_2O_2/H_2SO_4 oxidizer, and is referred to herein as a H_2O_2-DBFC.

This H_2O_2-DBFC offers several prospective advantages. First, the reactants can be stored at ambient temperature and pressure with concentrations of several molar, rather than as a high-pressure gas or cryogenic liquid. Second, when high reactant storage concentrations are combined with the 3.01 V theoretical cell potential for the $NaBH_4$/NaOH – H_2O_2/H_2SO_4 couple, the theoretical energy density and specific energy of the reactants surpass those of advanced Li-ion batteries [2]. Finally, DBFCs that consume stored H_2O_2 oxidizer can operate in anaerobic environments [9,10] (e.g. underwater or in space) and offer higher power density than systems that rely on O_2 due to the facile kinetics of H_2O_2 reduction.

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The desired electrochemical reactions occurring in a H_2O_2-DBFC are written in (R1)–(R3). The net cell reaction (R1) consumes BH_4^-, H_2O_2, OH^-, and H^+ and forms BO_2^- and H_2O for a standard cell potential $E^0_{R1} = 3.01$ V. The anode and cathode half-cell reactions are in (R2) and (R3), respectively. In (R2), BH_4^- and OH^- are electrochemically oxidized to BO_2^- and water. Electrons provided by (R2) travel through an external circuit to be consumed by the cathode half-cell electrochemical reduction of H_2O_2 and H^+ (R3).

$$BH_4^- + 8OH^- + 4H_2O_2 + 8H^+ \leftrightharpoons BO_2^- + 14H_2O \tag{R1}$$

$$BH_4^- + 8OH^- \leftrightharpoons BO_2^- + 6H_2O + 8e^- \quad E^0_{R2} = -1.246 \text{ V vs. RHE} \tag{R2}$$

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \quad E^0_{R3} = 1.763 \text{ V vs. RHE} \tag{R3}$$

Parasitic chemical reactions can also occur; they uselessly consume reactants and depress cell voltage by shifting concentrations near the electrodes. At the anode catalyst, when the supply of OH^- is insufficient, heterogeneous hydrolysis [11] converts BH_4^- to BO_2^- and H_2 via parasitic chemical reaction (R4).

$$BH_4^- + 2H_2O \rightarrow BO_2^- + 4H_2 \tag{R4}$$

Similarly, if the supply of H^+ in the oxidizer solution is insufficient, H_2O_2 undergoes heterogeneous decomposition at the cathode catalyst [12–14] to form water via the parasitic chemical reaction (R5).

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{R5}$$

Reactions (R1)–(R5) each summarize multiple elementary intermediate steps. For example, transferring $8e^-$ to the anode in reaction (R2) requires at least 8 elementary reactions. The microkinetics of elementary reactions occurring at a DBFC anode has been explored by Rostimikia et al. using density functional theory [15]. The rate determining elementary reactions and related kinetic parameters at the anode and cathode of a H_2O_2-DBFC are, however, still uncertain.

Experimental investigations of H_2O_2-DBFCs indicate that they do not meet their theoretical promise primarily because of transport limitations in the liquid reactant flow channels and the loss of fuel and oxidizer via parasitic chemical reactions at each electrode [11,16–19]. Unfortunately, the interdependencies of the H_2O_2-DBFC electrochemistry and parasitic reactions are difficult to decouple experimentally because of their complexity. Carefully constructed numerical models are well suited to such problems, because they can capture the complexity while revealing parameters that are inaccessible experimentally. We previously developed a numerical model to understand the relationships between cell geometry, operating conditions, and performance in an ideal H_2O_2-DBFC where all reaction rates were fast and parasitic reactions were omitted [20,21]. For this present work, we revise the existing model to include realistic reaction rates and parasitic reactions. Experiments with a H_2O_2-DBFC guide selection of appropriate global reactions for the model, and provide measurements to which the model is calibrated. The model is calibrated by fitting kinetic terms in the global reaction rates to H_2O_2-DBFC polarization curves measured over a range of BH_4^- concentrations. The simplified reaction mechanism in the revised model reduces the large number of uncertain kinetic parameters in comparison to elementary microkinetic models, and thereby makes fitting to measurements more tractable. With this simplification, the global reaction rates with fitted parameters can provide sufficient accuracy for cell-level studies as long as they reasonably capture the rate-determining processes.

Following calibration against the experimental H_2O_2-DBFC, the model is used to investigate the effects of parasitic reactions on H_2O_2-DBFC performance by examining a baseline case and then departures from the baseline with variations in fuel inlet concentration and flow rate.

2. Model development

A steady state isothermal H_2O_2-DBFC having the form shown in Fig. 1 was modeled with a 2-D finite volume approach. Aqueous fuel (1–50 mM $NaBH_4$/2 M NaOH) and oxidizer (10–40 mM H_2O_2/1 M H_2SO_4) flow through rectangular channels separated by a Nafion 117 membrane. Catalyst-coated channel walls constrain the flows and act as electrodes. BH_4^- is oxidized at the Au anode and H_2O_2 is reduced at the Pd:Ir cathode. Na^+ cations cross the membrane to charge balance the cell, bringing H_2O with them via electro-osmotic drag. The geometry in Fig. 1 represents a class of DBFCs having separated electrodes and membranes. Such DBFCs have been considered in earlier studies [22,23] because they are simple to fabricate, resist precipitate accumulation, expose the full membrane to the aqueous electrolytes, and orient the electric field so that it aids reactant transport [21]. This DBFC configuration can be represented in a computationally efficient 2D model, when the channel sidewalls are inert (electrochemically inactive) and spaced widely enough to have negligible effect on the hydrodynamics of the reactant flows. The model predicts cell current when the cell geometry, inlet flow rates, inlet concentrations, and cell voltage are specified.

Only a summary of the transport calculations and solution approach are provided herein because they have been described previously [20,21]. The reaction mechanisms and rates are discussed in detail because they are specific to this study.

2.1. Transport in the channels and membrane

State variables describe the reactant solutions for computational cells in each flow channel: pressure P, velocities v_x and v_y, electric potential ϕ, and species mass fractions Y_k. For the fuel solution species, $k = BH_4^-$, BO_2^-, Na^+, OH^-, H_2, or H_2O. For the oxidizer solution, $k = H_2O_2$, H^+, Na^+, SO_4^{-2}, H_2, O_2 or H_2O. The electrode-channel interfaces have state variables ϕ and Y_k, and the membrane–channel interfaces have state variables ϕ, Y_k and P. The value of each channel state variable is found by enforcing the associated conservation equation; conservation of mass (P), conservation of species (Y_k), conservation of momentum (v) and electroneutrality (ϕ). Solving for ϕ by enforcing electroneutrality implies that electrochemical double layers (the only regions in which substantial deviation from electroneutrality occur) are thin and effectively part of the electrode-channel interfaces. The interface values of P, ϕ, and Y_k are found by mass, charge and species flux matches, respectively. Fluxes due to electrode reactions and channel transport must match at electrode-channel interfaces, and fluxes due to membrane transport and channel transport must match at the membrane–channel interfaces. Mass, mole and charge densities are estimated using apparent molar solute volumes in the reactant solutions [21].

Boundary conditions at the inlets and outlets include fully developed momentum boundary layers ($\partial v_x/\partial x = 0$, $\partial v_y/\partial y = 0$) and no electric field in the x-direction ($\partial\phi/\partial x = 0$). Mass fractions are specified at the inlet (dictated by fuel and oxidizer concentrations) and pressure is specified at the outlet ($P = 0$). Boundary conditions at the electrodes include no-slip and impermeable boundary ($\nabla\vec{v} = 0$, $\partial P/\partial y = 0$). The anode is assigned $\phi = 0$, making it the