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Mathematical modelling of direct borohydride fuel cells

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HIGHLIGHTS

- ► The first detailed model of a direct-borohydride/oxygen fuel cell is developed.
- ► The performance is simulated and compared to experimental results.
- ► The performance on Pt and Ni anodes is simulated and the differences are explained.
- ► Extensions to the model are outlined.
- ► Key property values missing from the open literature are highlighted.

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ABSTRACT

A detailed mathematical model for the direct borohydride/O_2 fuel cell is developed. The activation polarizations, mass-transport limitations and resistances to charge transport in each component of the cell are explicitly incorporated. The anode kinetic mechanism is based on direct borohydride oxidation, borohydride hydrolysis and the full Tafel–Volmer–Heyrovsky mechanism for hydrogen evolution and oxidation. The mixed potential at the anode is calculated using the mixed-potential theory. The model results are compared to experimental data across a range of operating conditions and component properties, including the reactant concentrations, the anolyte flow rate, the ionomer volume fractions and the membrane/ionomer conductivity. A good qualitative fit to the experimental data is demonstrated. In order to gain insight into the anode reaction mechanism, the performance on both Pt and Ni anodes is simulated and compared to experimental observations. A detailed analysis of the results provides an explanation for the different performance on these catalysts.

1. Introduction

Direct hydrogen fuel cells have the potential to provide clean and sustainable power for a broad range of applications, from automotive propulsion to portable consumer electronics [1]. Cost effective and safe methods for sourcing, storing and handling hydrogen are key to the mass commericalisation of hydrogen fuel cell technology. Widespread adoption also requires radical changes to existing fuel infrastructures. In order to alleviate many of the problems related to the introduction of a hydrogen infrastructure, reformers can be employed to convert a hydrocarbon liquid fuel to hydrogen, but this introduces additional engineering complications and increases the costs, space requirements and weights of the fuel-cell power systems.

Replacing hydrogen with methanol is a potential solution to the aforementioned problems. Direct-methanol fuel cells (DMFC), on the other hand, suffer from methanol crossover and low open-circuit voltages (OCVs) [2], in part due to the inefficient anodic oxidation of methanol. The problems arising from the use of liquid methanol have led to a search for alternative hydrogen-carrier compounds, of which borohydride compounds are a prominent example [3]. A cell that utilizes a borohydride compound (usually sodium borohydride) as the fuel, a cation or anion exchange membrane and O_2 [4] or H_2O_2 [5] (in anaerobic environments) as an oxidant is termed a direct borohydride fuel cell (DBFC). A Schematic of the O_2 DBFC is shown in Figure 1.

DBFCs are characterized by their high OCVs (considerably higher OCVs than all other fuel cell technologies), low operating temperatures and high power densities [6,7]. These characteristics, in combination with their environmentally friendly by-products of reaction, have generated considerable interest in DBFCs. The cell power density and charge efficiency of DBFCs are strongly

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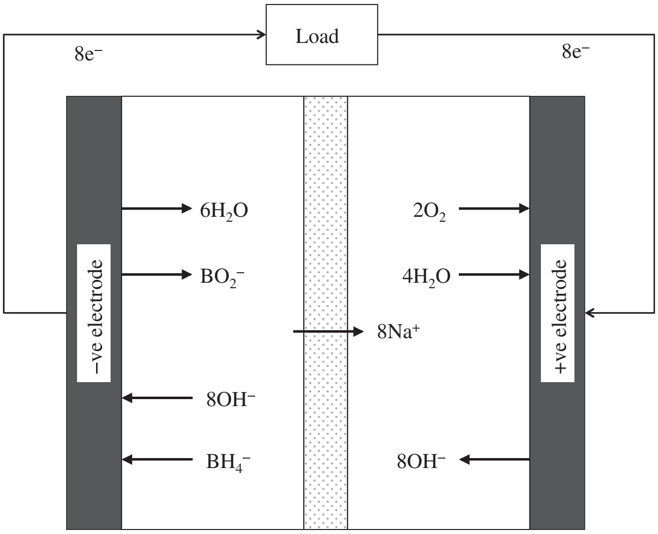

Fig. 1. Schematic of a direct borohydride fuel cell operating with O_2 as the oxidant.

influenced by the choice of anode catalyst. A complete (or close to complete) eight e^- anodic oxidation is feasible with Au and Ag electrodes [3,8,9], while Pt appears to liberate up to only four electrons [10]. One of the most appealing aspects of DBFCs is the ease with which the BH_4^- ions can be oxidised on non-precious materials such as Ni and Pd, as well as many common alloys used for hydrogen storage [7,10].

Amongst other factors, the electrode and support materials [7,10], the reactant concentrations [11,12], the PTFE/Nafion binder content in the anode [13,14], the operating conditions [11,15], the fuel pH [13], the diffusion layer properties [16], the membrane [7], the electrode structure [17] and the cell/stack design [7,10,18] influence the power density and efficiency of DBFCs. The anode materials, anolyte composition, membrane and operating conditions have a major effect on the evolution of H_2, which is an inherent feature of DBFCs. H_2 evolution, which can occur via at least two pathways, lowers the charge efficiency of the cell, inhibits reactant transport and poses safety concerns. The cathode performance is also not trivial. It has been demonstrated in several studies that the cathode polarisation is a major source of voltage loss [4,12,19], partly due to the establishment of a mixed potential resulting from borohydride crossover [20,21].

The performance of current DBFCs is highly encouraging, but further improvement and optimization are required. Amongst other considerations, there is ongoing research into the anode design, particularly with respect to suppressing H_2 evolution, examining and understanding the voltage losses under different design and operating conditions, and further understanding the anode and cathode reactions. In contrast to other types of fuel cells [22], there have been very few attempts to model DBFCs mathematically [23]. Verma and Basu [24] developed a highly simplified steady-state model of an O_2 DBFC to predict the cell voltage at a given current density. Activation overpotentials were estimated by inverting Tafel relationships and oxygen diffusion across a gas diffusion layer was incorporated by linearising Fick's law. Diffusion in the catalyst layer, which is the overwhelming source of mass transfer limitations, was neglected. Ohmic resistances were modelled by estimating an overall resistance from experimental data. To obtain a reasonable qualitative fit to experimental data, an ad hoc term representing the concentration polarisation in the anode was required. Sanli et al. [25] developed a series of similar models for a BH_4^-/H_2O_2 DBFC, ignoring mass, charge and heat transport. Concentration overpotentials were derived by including reactant concentrations inside a Tafel expression and by introducing a limiting current density. The ohmic losses were characterised by a constant resistance, estimated experimentally along with the reaction constants and the OCV. Only by including the cathode explicitly was a reasonable fit to the data possible. As in Ref. [24], a narrow range of current density was considered (up to only 0.02 A cm^{-2}). Models of this level of simplicity can provide a means for monitoring performance but lack sufficient physical detail for enhancing fundamental understanding of DBFC operation and for improving designs. Material properties, solution compositions, the complex reaction kinetics and the operating conditions are known to exert a strong influence on the performance of DBFCs. Incorporating these aspects of DBFC design and operation is key to developing effective modelling and simulation tools.

In this paper, a physics-based model for an O_2 DBFC is developed. The model incorporates the main factors affecting the cell voltage. Borohydride oxidation, hydrolysis and hydrogen evolution/oxidation are included in the anode mechanism. The full Tafel–Volmer–Heyrovsky mechanism is employed for the hydrogen evolution/oxidation reactions, together with competitive adsorption of H and BH_4^-. The mixed potential theory is employed to estimate the anode polarization. The predicted trends with respect to variations in key variables, including the reactant concentrations, the anolyte flow rate, the ionomer volume fractions and the membrane/ionomer properties, are then compared to experimental observations (from the open literature) and the results are analyzed and explained. The performance on a Pt/C anode and the performance on Ni anode are also simulated and compared. Explanations for the differences observed in the simulations (and in experiments) are proposed.

2. Mathematical model

Given a constant applied current density j_{applied}, the output of the model will be a value for the cell voltage. By varying j_{applied}, a polarization curve can be simulated. The cell voltage is calculated by subtracting the activation, ohmic and concentration polarisations from the OCV (at which the net current flow from the anode to the cathode is zero). The concentration polarisations are included in the activation polarisations by explicitly including the mass transfer resistances.

In the model developed, the cathode is considered to consist of a Pt/C and PTFE catalyst layer pasted onto a gas diffusion layer (GDL), in the form of a graphite paper. The anode consists of either Pt/C or Ni mixed with PTFE pasted onto a Ni foam. The electrodes are separated by a Nafion membrane. A schematic of the MEA is presented in Fig. 2. The cell is similar to that developed by Li et al. in Ref. [14] and where parameter values are available from that paper, they will be used in this study. It is important to point out that the focus of this study is to develop a physics-based framework for modelling DBFC and to validate the approach by capturing qualitative trends, rather than quantitatively fitting to experimental data. There is no loss of generality in this approach; once suitable data is available, together with all material properties, a quantitative fit would be straightforward to achieve.

Several simplifying assumptions were adopted in the development of the model. The main assumptions and their justifications are listed below.

1. The reactant concentrations are assumed to be spatially homogeneous in each component, although the main transport limitations are incorporated.
2. The generated H_2 gas forms gas bubbles, which travel at a different velocity from the bulk anolyte velocity; departures are induced by drag forces, equal in magnitude to the buoyancy