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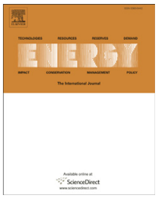

Partial modification of flow-through porous electrodes in microfluidic fuel cell

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ABSTRACT

The use of flow-through porous electrodes is identified as a promising approach to enhance the performance of microfluidic fuel cell (MFC). In this study, a dimensionless computational model is developed to analyze the distribution characteristics of the electrochemical reactions in flow-through porous electrodes of MFC. One important finding is that the electrochemical reactions mainly occur in the vicinity of the anode and cathode outlets. Based on this observation, the new design of partial modification at reactive sites is proposed to reduce the MFC cost. It is found that MFC with partial modification can achieve comparable performance with that of conventional full electrode modification, demonstrating the feasibility of partial modification method. The partial modification also offers a promising alternative to avoid unwanted secondary reaction, such as hydrogen evolution.

1. Introduction

The trend of miniaturizing technologies for mobile and low-power applications urges the development of microfluidic fuel cell (MFC). MFC is defined as a fuel cell with all components and functions confined to a microfluidic channel [1,2]. In MFC, the fuel and oxidant streams flow in parallel down a single microfluidic channel. The mixing of the streams is limited to transverse diffusion and an interfacial width at the center of the channel. The electrodes are integrated with sufficient distance from the mixing zone in order to prevent fuel crossover. Thus, unlike conventional micro fuel cells which use physical barriers (mostly proton-exchange membranes), MFC utilizes the occurrence of multi-stream laminar flow at the microscale to separate the fuel and oxidant streams. This unique membraneless architecture reduces the cost of the fuel cell and eliminates many membrane-related problems, including membrane degradation, fuel crossover, and water management. Various MFC designs have demonstrated the mechanisms using different fuels, oxidants, electrode materials and micro-channel configurations [2–5]. Among all of these studies, MFC with flow-through porous electrodes exhibits high power density (131 mW cm^{-2} at room temperature), owing to the high surface-to-volume ratio and thus more reaction interfaces in the porous electrodes [6,7].

Porous electrodes possess beneficial features for fuel cell systems. Currently, the most widely used porous electrode materials are carbon fibers, such as graphite felt, carbon cloth and carbon paper, due to their high electronic conductivity, lightweight matrix and low cost [8–14]. However, carbon fibers exhibit poor electrochemical activity [15,16]. Considerable attention has been given to modifications of carbon fiber electrodes to enhance their electrochemical properties [17–33], including chemical modification, electrochemical modification, thermal treatment, hydrothermal ammoniated treatment, metal compound coating, metal nanoparticle coating and so on. By incorporating additional treatments into the electrode preparation processes, the electrochemical activity of carbon fiber electrodes could be notably enhanced [24,33]. However, these methods are not favorable to practical applications due to the use of expensive novel materials and high energy consumption in the modification processes.

Another problem of modification of porous electrodes is possible occurrence of unwanted secondary reaction. Usually, the potential difference between the carbon matrix and the electrolyte solution at all points within the porous electrode should be high enough to initiate the electrochemical reactions, but not

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Nomenclature

a	specific surface area, m^{-1}
c	bulk concentration, $mol\ m^{-3}$
c^s	surface concentration, $mol\ m^{-3}$
c^f	reference concentration, $mol\ m^{-3}$
c_0	inlet concentration, $mol\ m^{-3}$
C	dimensionless concentration $=c/c^f$
C^s	dimensionless surface concentration $=c^s/c^f$
C_0	dimensionless inlet concentration $=c_0/c^f$
d	electrode length in the x direction, m
d_0	channel length in the x direction, m
d_1	modification region length in the x direction, m
D	diffusion coefficient, $m^2\ s^{-1}$
e	porosity
E^{eq}	equilibrium potential vs. SCE, V
E^{eq}_{cell}	equilibrium cell potential $= E^{eq}_c - E^{eq}_a$, V
F	Faraday constant, $C\ mol^{-1}$
g	dimensionless parameter $= \sigma_s/\sigma_l$
h	electrode height in the z direction, m
i	current density, $A\ m^{-2}$
i^0	exchange current density, $A\ m^{-2}$
i^L	limiting current density, $A\ m^{-2}$
I_s	dimensionless electrode current density $= -\gamma\nabla\varphi_s$
I_T	dimensionless total current density
j	local current density, $A\ m^{-2}$
J	dimensionless local current density $=\omega M$
k_m	mass transfer coefficient, $m\ s^{-1}$
L	electrode width in the y direction, m
M	dimensionless source term
n	number of electrons involved in reaction
Pe	Peclet number $=u_x d_0/D$
Q	charge source term, $A\ m^{-3}$
R	universal gas constant, $J\ mol^{-1}K^{-1}$
s	dimensionless parameter $=ai^0 d_0^2/nFDC^f$
S	species source term, $mol\ m^{-3}s^{-1}$
T	temperature, K
u_x	x component of velocity, $m\ s^{-1}$
$\vec{U}$	velocity vector, $m\ s^{-1}$
V	vanadium species
V_{cell}	cell voltage, V
x	distance in the direction perpendicular to fluid flow, m
X	dimensionless distance in the direction perpendicular to fluid flow
y	distance in the direction of fluid flow, m
Y	dimensionless distance in the direction of fluid flow
z	distance in the direction perpendicular to the x-y plane, m

Greek letters

α	charge transfer coefficient
β	$\alpha nF/RT$, V^{-1}
δ_1	ratio of modification region length to channel length $=d_1/d_0$
δ_x	ratio of electrode length to channel length $=d/d_0$
δ_y	ratio of electrode width to channel length $=L/d_0$
δ_z	ratio of electrode height to channel length $=h/d_0$
σ	electrical conductivity, $S\ m^{-1}$
τ	dimensionless parameter $= i^0/i^L$
η	overpotential, V
$\varnothing$	potential, V
φ	dimensionless potential $= \beta\varnothing$
φ^{eq}	dimensionless equilibrium potential $= \beta E^{eq}$
φ_{cell}	dimensionless cell potential $= \beta V_{cell}$
φ^{eq}_{cell}	dimensionless equilibrium cell potential $= \beta E^{eq}_{cell}$

Subscripts

a	anode
c	cathode
i	species, including fuel and oxidant
l	electrolyte
s	electrode
R	fuel in the anode
O	oxidant in the cathode

exceedingly high to avoid secondary reaction [34]. However, this potential difference can vary significantly in the electrode due to the ohmic potential drop within the porous structure. Therefore, secondary reactions, such as the hydrogen evolution, are often observed. They could dramatically affect the cell performance partly because the bubbling of hydrogen destructs the laminar nature of the flow [35–37]. For the fully modified electrode, the potential difference within the porous electrode is relatively high due to the enlarged current output and in turn the unwanted secondary reactions will become more likely to occur.

In this study, we aim to gain a better understanding on the working mechanisms of the porous electrodes and improve the MFC performance by exploring new electrode designs. A dimensionless model for MFCs with flow-through porous electrodes is developed for parametric studies with different electrode properties and operating conditions. There are two new contributions of the present study: (1) a systematical investigation on the detailed physical–chemical processes in the flow-through porous electrodes, including the charge/species transport and electrochemical reactions; and (2) development of new designs for the MFC porous electrodes to improve the cell performance. Based on our analysis, it is found that the proposed modifications of the porous electrode could effectively improve the MFC performance.

2. Model

2.1. Physical model

The 3-dimensional structure and 2-dimensional x-y view of the MFC using flow-through porous electrodes without modification are illustrated in Fig. 1(a) and (b), respectively. The computational domain consists of three regions: anode, middle channel and cathode. In this system, fuel in excess supporting electrolyte (e.g. 2 M V^{2+} in 4 M aqueous sulfuric acid solution as in [6]) is used as anolyte and oxidant in excess supporting electrolyte (e.g. 2 M VO_2^+ in 4 M aqueous sulfuric acid solution as in [6]) is used as catholyte. The two electrolyte streams containing fuel and oxidant are separately supplied to the fuel cell via the two inlets on both sides. They flow through the porous electrodes along the x-direction and meet in the middle channel. Electrochemical reactions take place at the interface between the electrode and electrolyte. At the anode, the fuel is oxidized and electrons are produced. The electrons flow along the y-direction to the external circuit via the anode current collector (covering the anode side surface: $y = 0$). At the cathode, the oxidant is reduced by the flow of the coming electrons from the external circuit via the cathode current collector (covering the cathode side surface: $y = 0$). After exiting the electrodes and