A counter-flow-based dual-electrolyte protocol for multiple electrochemical applications☆

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HIGHLIGHTS

- Certain hydrodynamic conditions ensure secondary counter-flow patterns.
- Multi-dimensional up-scaling strategy effectively increases overall energy throughput.
- Multiple dual electrolyte scenarios in fuel cells, electrolyzers and batteries could be enhanced.

ARTICLE INFO

ABSTRACT

This paper reports a computational demonstration and analysis of an innovative counter-flow-based microfluidic unit and its upscaling network, which is compatible with previously developed dual-electrolyte protocols and numerous other electrochemical applications. This design consists of multidimensional T-shaped microchannels that allow the effective formation of primary and secondary counter-flow patterns, which are beneficial for both high-performance regenerative H_2/O_2 redox cells and flow batteries at a low electrolyte flow-rate operation. This novel design demonstrates the potential to achieve high overall energy throughput and reactivity because of the full utilization of all available reaction sites. A computational study on energy and pressure loss mechanism during scale-out is also examined, thereby advancing the realization of an economical electrolyte-recycling scheme.

1. Introduction

In spite of the demonstrated marketability of proton-exchange membrane fuel cells (PEM) [1–3], their further deployment faces growing economic pressure because of the membrane cost and operating conditions. With its low-cost fabrication and mild operating condition, microfluidic fuel cell technology is regarded as a promising solution for a portable electricity source. Most current research efforts on microfluidic fuel cells focus on the pattern for which the laminar catholyte and anolyte streams flow in parallel [4]. The dual-electrolyte scenarios introduce favorable thermodynamics to multiple electrochemical processes. In the complicated and sensitive process of microfluidic electrochemistry, experimental operating conditions would be highly influential to efficiency, implying the importance of the reactor structure, microporous morphology and physical properties. As the design-based study is time-consuming though necessary for

performance optimization, rapid numerical screening is critical. System scale-out is another important application of the proposed numerical model due to the microfluidic system's robust yet low area-specific performance. With preliminary numerical investigation of the upscaling serpentine's pressure and mass distribution, an experiment-based scale-out could be more specific and effective. A typical example is a dual-electrolyte membraneless H_2/O_2 fuel cell proposed by Cohen et al. [5], where co-flow fluids in the microchannel could perform distinctive behaviors with high surface-to-volume ratios and super-fast mass transfer rates. The pH environments of anolytes and catholytes in the cell were optimized independently, demonstrating an open-circuit potential in excess of 1.4 V and a power density of 0.96 mW/cm² with oxidant dissolved in 0.1 M H_2SO_4 and hydrogen dissolved in 0.1 M KOH. The dual-electrolyte configuration not only rendered an elevated open-circuit voltage in the fuel cell mode but also allowed water electrolysis at a significantly reduced voltage [6]. Inspired by supreme

Nomenclature

		c	cathode
		i	species i
A	active area (cm^2)	u	velocity (m/s)
E	equilibrium potential (V)	V	voltage (V)
F	faradaic constant (C/mol)	α	transfer coefficient
g	gravitational acceleration (m/s^2)	γ	stoichiometric coefficients
i	current density (A/m^2)	τ	the viscosity stress tensor (Pa)
j	mass flux (kg/m^2·s)	μ	viscosity (Pa s)
M	molar mass (g/mol)	ρ	density (kg/m^3)
n	number of participating electrons	σ	conductivity (S/m)
n_t	number of electrons exchanged at the rate-limiting step	χ	reaction order
p	pressure (Pa)	φ	potential (V)
S_k	current source (A/m^3)	w	mass fraction
S_i	production or consumption rate (kg/m^3·s)	η	activation overpotential (V)
		m	main reaction
Subscript		p	parasitic reaction
		ref	reference
0	reference or boundary		
a	anode		

water-splitting performance, the integration of a dual-electrolyte technique in a microfluidic platform was applied to the electrochemical conversion of CO_2 to fuels. Freed from hindrances of the membrane structure and thermodynamic limitations, electrode potentials were drawn closer to the equilibrium status at higher reactivity. During the conversion of CO_2, the peak faradaic and energy efficiencies were monitored with noteworthy improvement and, hence, facilitate the motivation for a broader exploration [7–9].

Indeed, the natural mixing layer between the electrolytes could perform the same role as a physical barrier such as a proton-exchange membrane; however, retaining the characteristics of laminar flow requires a continuous electrolyte supply into the microchannel, leading to considerable electrolyte wastage and low electrolyte-utilization efficiency. To tackle this issue, this study employs a counter-flow design, which was initially proposed to provide effective electrolyte separation in a vanadium redox flow battery with multiple vanadium oxidation states [10] and further developed as a formic acid fuel-cell platform [11]. Fig. 1(a) shows a schematic of the counter-flow pattern with air-breathing electrodes. The fuel, formic acid, is dissolved in the anolyte, which is supplied from the right-hand inlet and oxidized at the porous anode. Similarly, the catholyte is introduced from the left-hand inlet, providing a reaction site for the gaseous oxidant penetrating the gas-diffusion anode. Unlike co-flow, the counter-flow pattern creates a mixing region, and the dominant viscous effect stabilizes the interface, preventing the interaction between the fuel and the oxidant [11–13]. The diffusion transfer is suppressed by the opposite convection transfer, and the diffusion time of reactive species is less than their convection

time, i.e. residence time. In this way, only a small electrolyte flow rate is required to form this virtual separating layer, allowing a high fuel-utilization operation.

The economic feasibility of microfluidic electrochemistry is also in doubt in spite of its high area-specific performance. Its practicability is severely constrained by the low overall yield due to the inherent reactor size. Dimensional scale-out has been proven infeasible [14] due to the boundary-layer growth and mixing-layer perturbation accompanied by significant energy losses. Other efforts, such as two-cell planar array [15], vertical stack [16], and multiplexing flow distribution [17], have suffered from low applicability to practical situations, where the fluid maldistribution is far more complex. Therefore, a new upscaling path needs to be developed for mass production and industrial applications. This could be achieved based on the above-mentioned microfluidic platform; our group [18] and others [19] have demonstrated its capability for efficient system scale-out. Based on these genetic mechanisms, a microfluidic multidimensional modularization design will be proposed. Performance losses during the scale-out will be minimized by an effective liquid-redistribution strategy. A two-dimensional shunt serpentine (Fig. 1(b)) and upscaling networks (Fig. 1(c)) will then be numerically established.

2. Numerical model

2.1. Basic assumptions

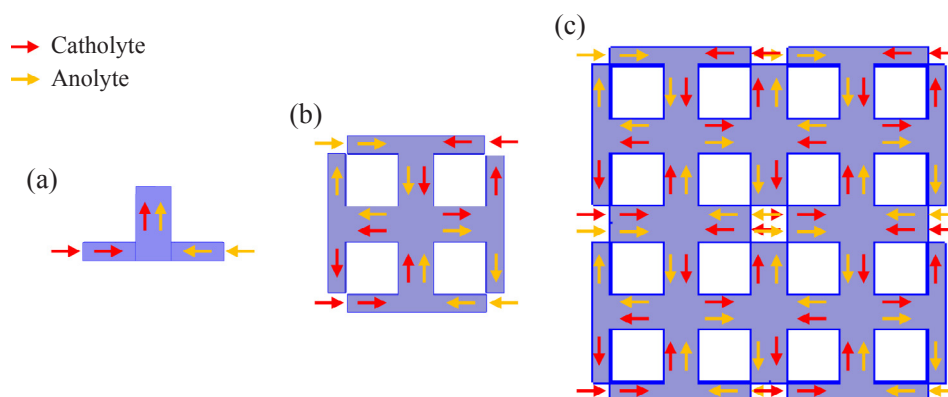The finite element analysis software, COMSOL Multiphysics, is used

Fig. 1. Schematics of counter-flow based fuel cell (a) unit, (b) module, and (c) up-scaling network.