

MICROFABRICATION AND PERFORMANCE EVALUATION OF MICROFLUIDIC MEMBRANELESS ENERGY CONVERSION DEVICES FOR HYDROGEN GENERATION AND UTILIZATION

Abstract

The typical electrolysis cell/ fuel cell components like membrane-electrode assembly (MEA), gas/liquid diffusion layer, and flow plates were eliminated by the strategic implementation of microfluidics. Microfluidic devices rendered membraneless operation owing to the prevalence of plane parallel flow in the microchannel. Hydrogen (H₂) production by water splitting in a membraneless microfluidic electrolysis cell (μ EC) allows flexibility in the choice of pH. An applied voltage induced a two-phase flow of gas products and liquid electrolyte in the μ EC microchannel. The gas products intermixing in the microchannel were averted by optimizing the electrolyte flow rate, which balanced the inertial and viscous forces acting on a fluid.

The development of the μ EC is limited by the complexity in fabrication the low hydrogen throughput, and gas purity in membraneless operation. The present research sheds light on the investigation and development of the μ EC that encompasses techniques to improve the reaction kinetics, ease the manufacturability, and enhance mass transfer in the microfluidic electrolysis cell to increase the hydrogen production rate with negligible gas crossover.

An asymmetric electrolyte configuration (acidic catholyte and alkaline anolyte) was used in the μ EC to drastically reduce the overpotential of water electrolysis by utilizing the electrochemical neutralization energy. The μ EC operating at 10 mA cm⁻² current density could electrolyze water at 1.58 V for the asymmetric electrolyte which was less as compared to that in acidic and alkaline electrolyte. The μ EC advancement was limited by the availability of a bifunctional catalyst compatible with microfabrication techniques. The scalable synthesis of a nickel nitride/ nickel (Ni₃N/Ni) bifunctional catalyst was demonstrated. Ni microelectrodes were microfabricated, and

nitridation and N-H grafting of the electrodes was achieved by ammonia plasma. The μ EC with $\text{Ni}_3\text{N}/\text{Ni}$ exhibited a current density of $263.73 \text{ mA cm}^{-2}$ at 2.5 V, a stable 6 h operation, and a performance efficiency of 99.86%. The multiple fabrication steps and low H_2 production rate impedes the scale-up of the μ EC for commercial application. The fabrication of the μ EC was elucidated, and the H_2 production increased by implementing a 3D-printed μ EC with flow-through porous electrodes. The μ EC attained an H_2 production rate of 15 mL min^{-1} with a current density of 748 mA cm^{-2} at 2.5 V. Accelerated stress testing was performed for 370 h with a fluctuating current density as a stressor. Minimum degradation of the electrodes was observed with a slight decrease in the performance of the μ EC. Negligible gas crossover at the optimized flow rate was observed in the μ ECs, which was analyzed by gas chromatography. The optimized flow rate of operation was obtained whereby, no gas intermixing takes place, by equating drag force acting on the gas bubble and opposing interfacial tension force at the triple phase boundary of electrode – gas bubble – liquid electrolyte interfaces in the direction of the flow.

The H_2 produced in the μ EC was consumed in a microfluidic fuel cell (μ FC) operating in tandem to generate micropower. In tandem operation, asymmetric electrolyte configuration could not be used due to opposite nature of operation of electrolysis cell and fuel cell. However, the results of the acidic and alkaline electrolyte were compared for the μ EC and tandem μ EC- μ FC operation. A voltage applied to the μ EC induces two-phase flow in the μ EC- μ FC, resulting in the evolution of H_2 and O_2 gases that are transported to the μ FC by convection, and consumed to generate power. The μ EC- μ FC delivered 14.68 mW cm^{-2} maximum power density with μ EC operating at 99.98% energy conversion efficiency and the μ FC attaining up to 50% fuel utilization with 4 h of stable tandem operation.

The outcome of the thesis paves the way for future research towards the scale-up of the μ EC for integration with renewable energy systems for on-site off-grid green hydrogen production.

Keywords: Microfluidics, microfabrication, thin-films, hydrogen, fuel cells.