

Understanding the Origins of Limiting Current in PEM water electrolysis

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論 文 内 容 の 要 旨

In recent decades, global climate change has made greenhouse gas reduction and reliable energy supply urgent priorities. Renewable energy sources such as wind and solar have attracted widespread attention due to their potential to address environmental and energy challenges. However, their intermittent nature limits their current contribution. Therefore, advanced energy storage technologies are essential to balance supply and demand. Among them, water electrolyzers offer a compelling solution by converting surplus renewable electricity into hydrogen gas as a clean energy carrier.

Among water electrolysis technologies, polymer electrolyte membrane electrolysis cells (PEMECs) stand out due to their ability to operate at high current densities, rapid start-up characteristics, and high hydrogen purity. However, components such as the iridium oxide catalyst and titanium porous transport layer (PTL) contribute to high capital costs, hindering the widespread commercialization of PEMECs. One effective strategy to reduce these costs is operation at even higher current densities, which enables reduction of the required electrode area and thus lowers the system cost.

However, high-current-density operation is limited by the so-called limiting current density (LCD), at which point the electrolysis voltage increases abruptly. This sudden voltage rise is generally attributed to mass transport limitations on the anode side. At the anode catalyst layer (CL), water is split into oxygen gas and protons. The generated oxygen gas, in turn, blocks access of liquid water to the CL. At high current densities approaching the LCD, oxygen accumulation in the PTL can severely inhibit water transport, resulting in further voltage increases. This indicates that gas-liquid transport in the anode compartment is a critical factor in PEM water electrolysis, especially near the LCD. A deeper understanding of the mechanisms behind the LCD can lead to optimized cell structures and operating conditions that support the operation at higher current densities and reduce system cost.

Many previous studies have investigated mass transport and electrochemical performance under moderate conditions, few have explored the severe limitations that arise at the LCD. At high current densities, gas-phase volume fractions become much higher than at lower current densities, requiring direct investigation. Moreover, prior research lacks a unified framework combining experimental data (e.g., polarization curves and bubble visualization) with numerical modeling.

In response to these challenges, this study conducts a quantitative analysis to clarify the mechanisms governing gas-liquid mass transport limitations at the LCD. First, a conventional PEMEC is used to determine the

LCD under varying cell temperatures and pressures, based on polarization behavior. In parallel, a one-dimensional two-phase flow model is developed to simulate gas–liquid transport within the PTL under LCD conditions. A visualization cell incorporating a glass window in the anode end plate is employed to observe bubble behavior in the flow channels using a high-speed camera. These observations, combined with structural variation of the PTL, reveal the correlation between bubble dynamics and PTL structure, and are used to define realistic boundary conditions for the developed model. Finally, a novel Pool-PEM cell equipped with a water reservoir is introduced to explore the LCD mechanism by analogy with the critical heat flux (CHF) phenomenon in pool boiling. By applying CHF theories such as hydrodynamic instability and capillary wicking, the behavior of gas–liquid at the LCD regime is quantitatively discussed. Details are as follows.

Chapter 1 introduces the background and motivation for the study, and it also outlines the methodology and strategy to investigate the LCD in water electrolysis.

Chapter 2 experimentally and theoretically investigates the influence of operating temperature and pressure on gas–liquid two-phase flow behavior under LCD conditions in a conventional PEMEC. A combined approach using polarization curve measurements and one-dimensional two-phase flow simulations clarifies the relationship between mass transport limitations and the onset of the LCD. It is found that the LCD occurs when the water saturation near the catalyst layer approaches zero, at which point bubble overvoltage sharply increases, showing consistency with I–V curve behavior. In addition, it is revealed that lower operating temperature and higher pressure reduce the volume of generated oxygen gas and promote water supply to the CL, thereby increasing the LCD.

Chapter 3 focuses on the influence of PTL structure on bubble dynamics and LCD. A custom-designed visualization cell with a glass window embedded in the anode end plate is employed to observe bubble behavior, particularly at the interface between the PTL and flow channel. It is revealed that PTL with a higher porosity significantly reduces bubble accumulation at this interface. The PTL with higher porosity is shown to have more straight pores and more bubble detachment sites, resulting in reduced mass transport resistance and enhanced LCD. Under conditions of 80 °C and 0.1 MPa, experimental results show that increasing porosity from 45% to 72% results in a 48% increase in LCD. The boundary conditions refined through the observation are embedded in the model developed in Chapter 2, leading to more accurate LCD predictions.

Chapter 4 introduces a newly developed Pool-PEMEC with a novel structure designed to investigate the LCD mechanism by drawing an analogy to the critical heat flux (CHF) in pool boiling. This cell features a water reservoir, allowing water to be supplied without the forced convection flow. In this configuration, CHF-based theories such as hydrodynamic instability and capillary wicking, previously used for CHF estimation, are applied to interpret LCD behavior. The experimentally observed LCD reached 6.6 A cm^{-2} . However, the predicted values by the hydrodynamic instability theory markedly differed from the experimental results. On the other hand, a capillary wicking model provided more reasonable predictions. This suggests that the mass transport limitations in the PTL occur prior to the onset of hydrodynamic instabilities and significantly influence the LCD.

Chapter 5 summarizes all the findings and outlines potential directions for future research.