From the Dynamics of H_2 and O_2 Bubbles at μ-Electrodes towards Membraneless Electrolyzers

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Abstract

Understanding bubble dynamics and multiphase flow in electrolyzers is important to improve the insufficient energy conversion efficiency of low temperature electrolyzers. In this talk I give an overview over relevant phenomena on different length scales. Starting with Platinum-microelectrodes as model for catalytically active sites, I discuss characteristic features of the evolution of both hydrogen and oxygen bubbles. A focus is on the various modes of Marangoni convection, which significantly change the heat and mass transfer. For nickel-based macroelectrodes I next show how the morphology of the electrode, affecting both the electrochemically active surface area and the wettability, modifies the bubble size distribution produced. Finally, on the scale of small membraneless electrolyzers, features of the multiphase flow are discussed in relationship to the electrolyzer performance. Finally, an outlook to unresolved issues is given.

Keywords: water electrolysis, hydrogen, oxygen, bubbles, Marangoni flow, membrane-less electrolyzer

Introduction

Water electrolysis, powered by a grid containing large fractions of renewable energies, is the key technology to produce green hydrogen, which is needed to approach a low-emission-industry. However, the success of this transformation depends crucially on both the costs of electric energy and the energy conversion efficiency of the various electrolyzers. In low-temperature electrolyzers, gas bubbles are generated by the hydrogen evolution reaction and oxygen evolution reaction. These bubbles reduce the energy efficiency of electrolyzers by creating bubble-induced overvoltages [1], resulting from blocking active catalytic sites and increasing the ohmic resistance. An efficient bubble management to minimize bubble-induced overvoltages seeks to suppress bubble nucleation in undesired part of the electrolyzer, facilitates rapid bubble detachment from active sites and a subsequent fast transport through the electrolyzer structure. Precondition is a solid understanding of the dynamics of hydrogen and oxygen bubbles and the underlying forces. This understanding is used in the design and testing of membraneless flow-through electrolyzer in which bubbles are efficiently transported by the flow from nickel mesh electrodes. For a novel Y-shaped membraneless electrolyzer insights into the multiphase flow therein are given.

Methods

Different types of experiments are presented using either Pt microelectrodes or various types of nickel electrodes, blank or structured; operated both in potentiostatic or galvanostatic mode. These experiments are conducted by simultaneously applying various optical methods, including high-speed shadowgraphy, particle tracking velocimetry (PTV) to obtain the velocity field around the bubbles, Schlieren imaging to visualize the refractive index field around the bubble and far-field microscopy to measure the bubble size distribution.

Results and Discussion

Significant progress has been made in understanding the forces acting on hydrogen and oxygen bubbles and their subsequent growth regimes [2], including the discovery of new oscillatory regimes across various potentials and electrolyte concentrations. This advancement has been facilitated by adapting a new schlieren technique [3], which enables the temperature and concentration fields around the H_2 and O_2 bubbles to be measured in-situ. By applying synchronously particle image velocimetry, a comprehensive understanding of Marangoni convection at the base of H_2 and O_2 bubbles has been achieved. The convective patterns around H_2 and O_2 bubbles, and hence the temperature distribution, show distinct differences. Furthermore, the Marangoni convection divides into two regimes: the fast thermo-capillary Marangoni convection associated with the Joule heating due to the high current densities, and the slower soluto-capillary Marangoni convection, induced by concentration gradients [4]. The latter are created either by proton consumption in the case of the hydrogen evolution reaction, or by proton production during O_2 evolution, under the constraint of electro-neutrality.

Understanding the forces acting on these bubbles is used to elaborate strategies to reduce bubble-induced overvoltages, and to improve the energy efficiency of alkaline electrolyzers. These strategies include optimizing electrode wettability through surface structuring [5], as well as exploring alternative, membraneless electrolyzer architectures and the bubble size distribution therein [6].

Conclusion

In this work we summarize the present status of understanding of the main features of H_2 and O_2 bubbles growing at microelectrodes. While the thermocapillary convection emerging during the bubble growth is meanwhile well understood, numerous questions on its solutocapillary pendant currently remain open. The same holds true for the electric force acting on the bubble due to its surface charge. Furthermore, it is shown that changes in the wettability of the electrodes, e.g. via micro- and nano-texturing, have a significant impact on bubble nucleation and the resulting bubble sized distributions. Finally, advantages and disadvantages of membraneless electrolyzers are discussed, where the electrolyte flow is used to separate the products and to facilitate an optimized bubble management.

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