Boiling impact on acid water electrolysis process: fundamentals to application

李, 林軍

出版情報：Kyushu University, 2022, 博士（工学）, 課程博士
バージョン：

（様式２）

氏　　名　：LI LINJUN（リ　リンジュン）

論文題名　：Boiling impact on acid water electrolysis process–fundamentals to application–

（酸性水電解プロセスにおける沸騰の効果～基礎から応用～）

区　　分　：甲

論 文 内 容 の 要 旨

The problem of environmental pollution and fossil fuel depletion motivates us to introduce renewable energy such as solar and wind. However, the renewable energy source rather unevenly spreads and electricity generation from the sources fluctuates. Hydrogen energy society can compensate for this drawback, where hydrogen produced through water electrolysis powered by renewable energy has a role of energy media.

Among several types of water electrolysis cells, polymer electrolyte membrane water electrolysis (PEMWE) has advantages: high power density, fast dynamic response, and high hydrogen purity. These advantages make PEMWE more competitive in the hydrogen energy society expected. However, the initial cost of PEMWE is expensive and disturbs widely-spreading use of PEMWE. Reducing the initial cost of PEMWE is urgent issue to address.

De-Donder equation derived from the second law of thermodynamics suggests that boiling superimposed on water electrolysis possibly reduced the electrolysis voltage. Once the boiling can decrease the voltage, the decreased voltage can be converted to a higher current density operation, leading to a less electrode area and less CAPEX of PEMWE. Based on this scenario, a previous study [K. Ito et. al., ECST, 2017, 80(8): 1117-1125.] examined the boiling effect with a practical and lab. scale PEMWE, and then found out that the electrolysis voltage near the boiling point was approximately 100 mV smaller than that under less and far beyond the boiling point, implying that the boiling effect exists. However, the previous study did not clarify the boiling effect’s mechanism: where and how the boiling reduces the electrolysis voltage.

Understanding the boiling effect's mechanism and maximize the boiling effect is the target of this study. A three electrodes cell experimentally elucidates which overpotential component can be reduced by the boiling. A heater was embedded in the working electrode (WE). Different mass transport resistance component was built on the surface of the WE. These specific apparatuses provided enables the WE to reach the boiling point temperature and can separate overvoltage components (Nernst loss and activation overpotential) in oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER). Besides, a theoretical analysis performed, where the experimentally-obtained boiling effect was quantitatively examined. Theoretical analysis revealed that decreasing the dissolved gas concentration (oxygen and hydrogen in the case of OER and HER, respectively) at electrode is a key for the boiling effect. Finally, the developed model was applied to the case of a practical PEMWE and simulation based the model agreed with the boiling effects appeared in the PEMWE. Detail is as follows.

Chapter 1 explains the role, current status, and issues of water electrolysis, and introduces the boiling effect and strategy for how this study clarifies the boiling effect.

Chapter 2 experimentally examined the boiling effect on OER with three WEs, so-called WE1, WE2, and WE3. The WEs with different structure has different oxygen mass transfer resistances. WE1 comprises only a CL directly facing electrolyte. WE2 embeds a PTL on the CL. WE3 has a flow channel in addition to the PTL. The last one has the largest oxygen transport resistance. These successive experimental analyses found that a considerable amount of vapor generated by boiling dilutes the oxygen gas and dissolved oxygen gas in the CL, and decrease the Nernst loss in OER. Also, it is clarified that the phenomenon triggered by boiling is enhanced when the oxygen mass transfer resistance is high.

Chapter3 established a theoretical model to quantitatively understand the boiling effect on OER. The model includes OER reaction with charge conservation, mass and momentum conservation considering gas/liquid flow in the PTL. Theoretically predicted OER overpotential agreed with experimental value and revealed the scenario of boiling effect: boiling significantly reduces the oxygen partial pressure in bubbles of oxygen gas and vapor mixture, the bubbles attract the dissolved oxygen gas surrounding the bubbles, thereby reducing both the partial pressure and dissolved concentration of oxygen gas and leading to smaller Nernst loss and OER overpotential. It is worth to mentioned that the OER under the bubble by boiling is activated and OER current contribution ratio is significantly improved.

Chapter 4 experimentally and theoretically investigated the boiling effect on HER. The experimental methodology and theoretical method for HER were similar to those for OER. The boiling effect on HER was also similar to that on OER. The boiling superimposed on HER accelerates liquid water and gas velocity in PTL and enhances HER mass transfer. Moreover, the boiling lowers the hydrogen partial pressure in the bubbles and the dissolved hydrogen concentration surrounding the bobbles, resulting in a smaller HER overpotential.

Chapter 5 challenged to clarify how the boiling effect works in a practical PEMWE and reduces electrolysis voltage. Because the PEMWE composes all components for both OER and HER, a theoretical model here developed composes them all, and can predict every overpotential: ohmic overpotential for polymer electrolyte membrane, and Nernst loss and comprehensive activation overvoltage for both OER and HER. The theoretical prediction qualitatively agreed with experimental results and revealed that the boiling effect also functions in the case of practical PEMWE. The water vapor produced by boiling significantly reduces the Nernst losses at the anode and the cathode. The ohmic overpotential, which is a problem in the practical PEMWE case, does not increase at boiling point, but abruptly rises when PEMWE enters drying conditions far beyond the boiling temperature. As for a representative result, it is suggested that boiling can increase the electrolysis efficiency by about 5% at 0.5 $A \cdot cm^{-2}$.

Finally, chapter 6 concludes this study, and indicates possible future works.