



Engineering electrode wettability to enhance mass transfer in hydrogen evolution reaction

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ABSTRACT

In hydrogen evolution reaction, inefficient mass transfer caused by bubble adhesion on electrode, bubble dispersion in electrolyte and slow H₂ diffusion, has greatly impeded the reaction process. Existing techniques can only resolve bubble adhesion or bubble dispersion problems. Strategy that simultaneously solve bubble adhesion, bubble dispersion and poor hydrogen diffusion problems is rarely reported. Recently, an article reported a new electrode with special wettability design, which can efficiently promote bubble transfer and dissolved H₂ diffusion. This design can simultaneously solve above mentioned three mass transfer issues and improve electrode efficiency. We summarize the remaining challenges of this work and outlook potential approaches to promote mass transfer in gas-evolution reactions.

KEYWORDS

hydrogen evolution reaction, wettability, bubble, mass transfer

Electrocatalytic hydrogen evolution reaction (HER) is considered as an effective method to produce green hydrogen, which will play significant role in low-carbon future [1-3]. Typically, HER in acid media includes three critical steps (Fig. 1(a)) [4, 5]: i) H⁺ transfer from electrolyte to electrode interface; ii) electrocatalytic reactions at electrode surface; iii) mass transfer of H₂, including dissolved H₂ diffusion and gaseous bubble motion. The majority of studies have focused on step 2 and designing elegant electrocatalysts to improve HER efficiency [6, 7]. However, especially at large current density, the performance of HER is greatly impeded by inefficient mass transfer of H₂, i.e., bubble adhesion on electrode (Fig. 1(b)), bubble dispersion in the vicinity of electrode (Fig. 1(c)), and poor dissolved H₂ diffusion (Fig. 1(d)) [8]. The adhered hydrogen bubbles on electrode surface will isolate catalytic active sites from the electrode and block electrolyte diffusion [9], and the dispersed bubbles in the vicinity of electrode will occupy the electrolyte volume and cause additional ohmic resistance as well [10]. Meanwhile, the critical concentration of dissolved H₂ required for bubble nucleation is ~310 times larger than the saturation concentration at room temperature and pressure [11], which will cause large concentration overpotential [12].

Active bubble detaching methods have been developed to remove bubbles from electrode surface, such as flow cell [13], magnetic field [14], ultrasonic field [15] and super-gravity field [16]. But these active bubble detaching methods not only require additional equipment and energy input, but also leave bubble dispersion and poor dissolved H₂ diffusion problems.

Given the typical bubble formation procedures of nucleation, propagation and adhesion, aerophobicity-based passive bubble detaching methods were designed to promote bubble detachment. For example, Sun et al. reported a kind of superaerophobic electrode which can offer a rapid removal of small gas bubbles and constant working area, resulting in promoted electrocatalytic performance [17]. Although without extra equipment and energy input, these superaerophobic electrodes still cannot resolve the bubble dispersion and poor H₂ diffusion issues. In 2016, Yu et al. reported a “transporting strategy”, i.e., utilizing aerophilic conical electrode to achieve directional bubble transportation and collection during HER [18]. This directional transportation ability is benefitted from geometry gradient of cone shape and large bubble adhesive force of aerophilic electrode surface. With this strategy, bubble dispersion has been well resolved, but bubble adhesion and H₂ diffusion problems still exist.

Recent reporting in Science Advances (<https://www.science.org/doi/10.1126/sciadv.add6978>), Cunming Yu, Lei Jiang and their colleagues have developed a superaerophilic/superaerophobic cooperative electrode to enhance mass transfer through simultaneously solving bubble adhesion, bubble dispersion and poor hydrogen diffusion problems as shown in Fig. 2 [19]. The electrode was composed of superaerophilic (SAL) stripes and superaerophobic (SAB) electrocatalytic region (Fig. 2(a)). The SAL stripes were covered by gas cushion and acted as gas channel to transport H₂. At

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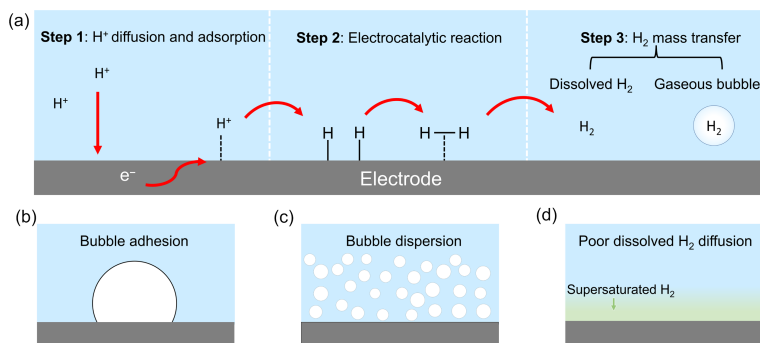


Figure 1 Schematics of HER process in acid electrolyte and H₂ related mass transfer issues. (a) HER process in acid electrolyte. (b) Bubble adhesion, (c) bubble dispersion and (d) poor dissolved H₂ diffusion issues in HER.

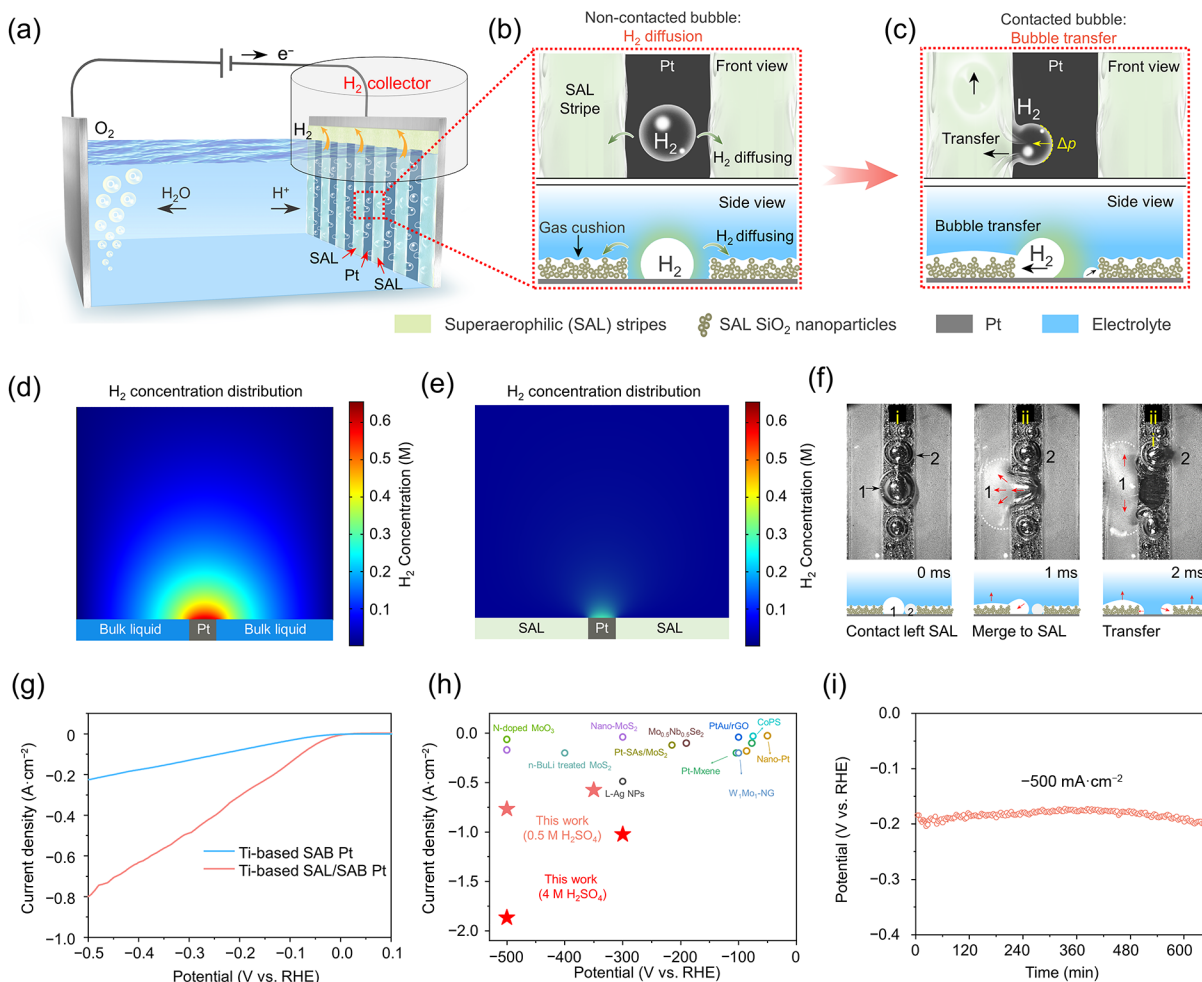


Figure 2 Superaerophilic/superaerophobic cooperative electrode. (a) Schematic of flat Pt electrode with SAL stripes. (b) Schematic of H₂ diffusion of non-contacted bubbles. The dissolved H₂ can diffuse out the reaction system through superaerophilic (SAL) stripes. (c) Schematic of bubble transfer of contacted bubble. As growing up, the bubble contact SAL stripes and be timely transferred. (d, e) Simulated H₂ concentration distribution at flat Pt electrode without (d) and with (e) SAL stripes. (f) Optical images of bubble transfer process on electrode with SAL stripes. (g) LSV plots of Ti-based superaerophobic (SAB) Pt electrode and Ti-based SAL/SAB Pt. (h) Comparison of the current densities of the Ti-based SAL/SAB Pt electrode with various 2-dimensional electrode. (i) Stability test of Ti-based SAL/SAB Pt electrode in 4 M H₂SO₄. (a)–(i) Adapted with permission from Ref. [19], © 2023 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science.

beginning of HER, H₂ bubbles will not contact SAL stripes, but the dissolved H₂ molecules can directly diffuse to ambient air through gas cushion at SAL stripes, which is connected with ambient air (Fig. 2(b)). When bubbles grow up and contact with the SAL stripes, H₂ bubbles will be rapidly transferred through SAL stripes, owing to the asymmetric Laplace pressure between electrocatalytic region and SAL stripes. Consequently, bubble adhesion and direct H₂ bubbles releasing in electrolyte is greatly avoided (Fig. 2(c)).

The enhancement of H₂ diffusion was verified by finite element modelling. As shown in Fig. 2(d), electrode without SAL stripes showed extremely high dissolved H₂ concentration (~0.66 M) at electrode surface. After introducing SAL stripes (Fig. 2(e)), the H₂ diffusion distance was dramatically decreased to achieve a much lower H₂ concentration compared to the electrode without SAL stripes. Fast bubble transfer in milliseconds can be directly observed in Fig. 2(f). Benefitted from above mentioned

enhancements, the Ti-based SAL/SAB cooperative Pt electrode achieved $-10 \text{ mA}\cdot\text{cm}^{-2}$ at overpotential of -19 mV , while for Ti-based SAB Pt electrode, the required overpotential was -49 mV (Fig. 2(g)). With optimizing electrolyte concentration, the Ti-based SAL/SAB Pt electrode achieved ultrahigh current density ($-1,867 \text{ mA}\cdot\text{cm}^{-2}$) at overpotential of -500 mV , which is almost the best in recent reported 2-dimensional electrode. And the Ti-based SAL/SAB Pt electrode exhibited stable HER in $4 \text{ M H}_2\text{SO}_4$ for over 10 hours.

Remaining challenges in this research are experimental evidence of dissolved H_2 diffusion and stability at large current density. At the moment, the enhanced H_2 diffusion is verified through finite element modelling and without direct experimental investigation. To further elucidate the intrinsic mechanism of dissolved H_2 diffusion on SAL/SAB cooperative electrode, more *in-situ* experimental evidence needs to be explored. And stability performance at $500 \text{ mA}\cdot\text{cm}^{-2}$ is far below the industrial level, which also need to be improved in future.

With the development of bubble super-wettability system, wettability design has showed great potential in gas-involved electrode [20, 21]. There are several research directions can be explored to promote bubble related mass transfer in gas-evolution reaction: 1) exploring catalysts with special micro/nano structure to delay bubble nucleation and accelerate bubble detachment; 2) designing single or multi-wettability pattern to promote bubble transfer or dissolved molecules diffusion; 3) developing new methods to fabricate stable catalysts and superaerophilic coatings. In addition, the feasibility of applying the superaerophilic/superaerophobic cooperative strategy in other gas-involved reactions need to be explored in future researches.

Declaration of conflicting interests

The authors declare no conflicting interests regarding the content of this article.

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