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Nanoarray based "Superaerophobic" Surfaces for Gas Evolution Reaction Electrodes

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Electrochemical gas evolution reactions are now of great importance in energy conversion processes and industries, and the keys for improving the catalytic performances lie in developing efficient catalytic electrodes. Besides the exploration of highly active catalysts, fast removal of the gas products on the electrode surface should be realized because the adhered gas bubbles would block the following catalytic reactions and decrease the efficiency. In this paper, we introduced an ideal structure, "superaerophobic" surface, to diminish the negative effects caused by the adhered gas bubbles. Several recent works focusing on addressing this issue are presented with the target reactions of hydrogen evolution and oxygen evolution. It is demonstrated that micro/nano-engineering of the catalyst directly on the current collector is a promising approach to minimize the negative effective induced by the gas bubble adhesion. At the last section, we have also discussed the promise of this methodology for other energy related systems.

1. Introduction

Gas evolution reactions (GERs), which are processes of converting liquid reactants to gas products accompanied with electrons transfer in aqueous mediums, are of great importance in various industries, covering a number of energy storage and conversion systems. Hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are two essential components for electrochemical water splitting, which is considered as one of the most effective approach for future energy solution.[1, 2] In addition, OER is also crucial in the charge process for rechargeable metal-air batteries[3, 4], and HER is necessary for chlor-alkali industry[5] as well as chlorine evolution reaction (ClER). GERs also hold keys in anodic reactions in direct liquid fuel cells, such as methanol oxidation and hydrazine oxidation.[6-8]

For the above mentioned GERs, catalysts are required to reduce the overpotentials for achieving high reaction rates (i.e. high current densities). Constructing ideal catalytic electrodes for GERs should follow three principles. Firstly, for each target reaction, the catalyst selected should possess a high intrinsic activity, which is determined by the electronic structure of the active center.[9-16] Secondly, the catalyst film should be porous and with high electric conductivity, which permits the penetration of the electrolyte and accelerates the electron transfer throughout the whole electrode.[17-19] Thirdly, the surface of the catalytic electrode should be easy to release the as-formed gas bubble product because severe adhesion of the gas bubble will block the contact between the catalyst and reactant, cause excessive ohmic drop and thereby decrease the efficiency.[20] Although it is reported that inducing ultragravity[21] or ultrasonic treatment[22] is beneficial to the disengagement process of gas bubbles, however, they are not cost-effective for industrial production.

This review summarized several recent works focusing on nanoscale electrode surface engineering to address the third principle of constructing an efficient catalytic electrode, which simultaneously meets the first and second principles. It is demonstrated that micro/nano-engineering of the catalyst directly on the current collector to gain a low-adhesion electrode is a promising approach to minimize the negative effective induced by the gas bubble adhesion. A new concept, "superaerophobic" surface, is introduced to describe the interaction between gas bubbles and the low-adhesion electrodes. HER and OER are the target reactions shown here, and the optimized architectures for the various catalysts are presented. At the last section, the promise of this methodology for GERs in other systems is also discussed.

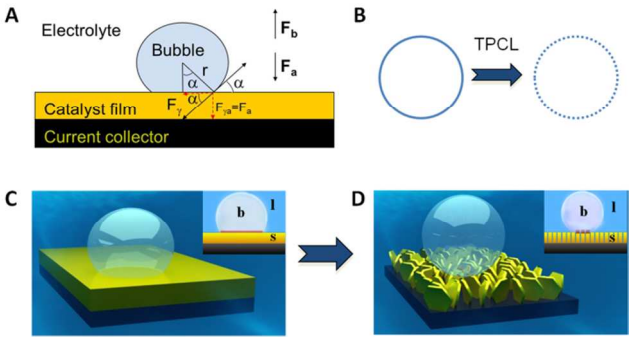

Figure 1. (A), force analysis of a single gas bubble sitting on the catalyst film; (B), triple-phase contact lines (TPCLs) on the flat film (left) and nanostructured film (right); (C) and (D), schematic illustration of the adhesion behaviors of gas bubbles on flat film (left) and nanostructured film (right). Inset: side views to show the different intact and discontinuous TPCL on flat and nanostructured films, also the different contact angles. The brown zone is "dead area" isolated by as-formed bubble. (Reprinted with permission from Ref. [20], Copyright 2014, Wiley-VCH)

2. Mechanism to design low-adhesion electrodes

As the reactant is liquid and the product is gas in GERs, a three-phase interface is formed together with the solid electrode, as shown in Figure 1A. If the as-formed gas bubbles melt and form a gas film, the electrolyte diffusion to the electrode surface will be blocked. Accordingly, the electrode surface should be able to readily release gas products. Thus, how to make the surface dislike the gas product is the main challenge in constructing the architecture of the catalyst film. For a single gas bubble sitting on the surface of catalyst film (Figure 1A), it suffers two main forces: one is the buoyant force (F_b) that is proportional to the volume of the gas bubble assuming that the shape of the gas bubble is a complete sphere (equation 1); the other is the adhesion force (F_a) from the catalyst film underlying, which can be expressed as equation 2. The gravity of the gas bubble is neglected because of the much smaller density of gas relative to that of the liquid. If the gas bubble is going to be detached from the surface, the buoyant force should become large enough to match with the adhesion force (equation 3). Therefore, theoretically, the releasing diameter of the gas bubble is dependent from the adhesion force from the catalyst film. Derived from the equations 1-3, the radius of the gas bubble is proportional to the product of the root of γ and sine function of α (equation 4).

$$F_b = \rho \cdot g \cdot \frac{4}{3}\pi \cdot r^3 \qquad \text{Eq. 1}$$

$$F_a = \gamma \cdot 2\pi(r \cdot \sin\alpha) \cdot \sin\alpha \qquad \text{Eq. 2}$$

$$F_b = F_a \qquad \text{Eq. 3}$$

$$r \propto \sqrt{\gamma} \cdot \sin\alpha \qquad \text{Eq. 4}$$

Where ρ is the density of the electrolyte, g is the gravitational acceleration, r is the radius of the gas bubble, γ is the surface tension of the catalyst film and α is the angle between horizontal direction and the tangent direction of the contact point of gas bubble and catalyst film.

The adhesion force originates from the triple phase (solid-liquid-gas) contact line (TPCL), which is a continuous circle for an absolutely flat film (Figure 1B, left). Constructing nanostructured film can offer a much rougher surface, which significantly decreases the surface solid fraction and thus cuts the TPCL into discontinuous dots (Figure 1B, right). Given that each point of the TPCL possesses the same adhesion force to the gas bubble for the same material, the broken TPCL would show a much smaller accumulated adhesion force relative to the continuous TPCL. Moreover, direct growth of the nanostructures can bring about many other advantages, such as good electron transportation and high porosity, which make the catalyst film more conductive and facilitate the penetration of electrolyte (reactant), leading to the improvement of catalytic performance.

3. Realization and demonstration of low-adhesion electrodes

3.1 Hydrogen evolution reaction (HER)

HER is a typical example of GERs, as it has a variety of applications for energy conversion processes.[23, 24] This reaction needs catalysts to reduce the overpotential to operate this reaction, and the activities of the catalysts are highly dependent on their electronic structures.[25-27] About a decade ago, MoS_2 was emerged as an efficient catalyst for HER due to the suitable binding energy to hydrogen (not too strong or not too weak) at the edge sites, thus the Mo edges are considered as active sites for MoS_2.[13, 28-33] Recently, many compounds have been synthesized and identified with superior HER activities because of the new active sites, such as WS_2[34], $CoSe_2$[23], CoS_2[35, 36], NiP[37], CoP[38, 39], Mo_2C[40], MoB[41] and so on. More recently, metal free catalysts are also investigated with high HER performance.[42, 43] To further optimize their HER performance, rational design of the structures of the catalysts are now being actively pursued.[44]

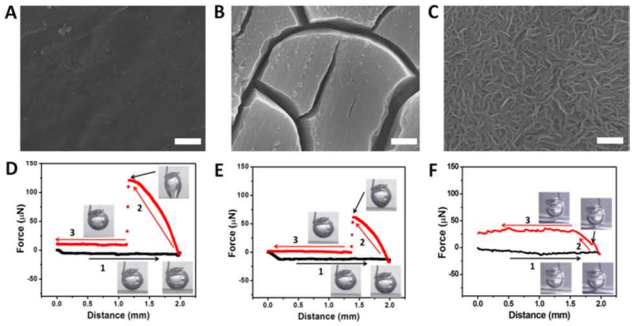

Figure 2. (A), (B) and (C), the different surface morphologies of MoS_2 films; (D), (E) and (F), the corresponding gas bubble adhesion forces of the above surface structures. (Reprinted with permission from Ref. [20], Copyright 2014, Wiley-VCH)

Our group has employed MoS_2 as the electro-catalyst to demonstrate the effectiveness of the low-adhesion surface according to the structural designing.[20] Three MoS_2 films with different surface architectures (nanostructured, microstructured and flat films) were fabricated by *in-situ* sulfidation and precipitation processes, as shown in Figure 2A, B and C. The adhesion force measurements revealed that the flat film exhibited a strong interaction to the gas bubble while the nanostructured film showed a negligible response (Figure 2D-F), indicating that constructing nanoporous surface was an efficient approach to reduce the adhesion force towards gas bubbles. In addition, the contact angle of a gas bubble on the nanostructured surface is larger than 150°, thus making the surface with low adhesion force (equation 2) and "superaerophobic".

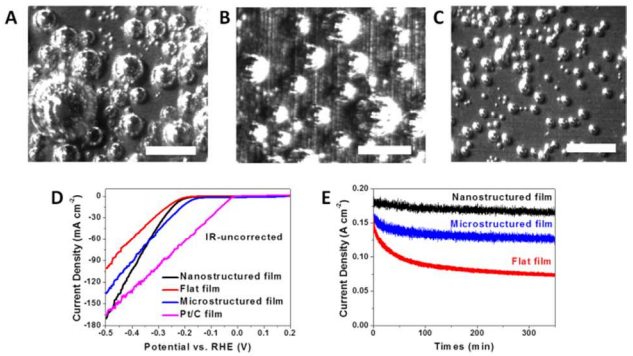

Figure 3. (A), (B) and (C), different gas evolution behaviors on the flat, microstructured and nanostructured MoS_2 films; (D), HER performances of the 3 MoS_2 films and commercial 20 wt%

Pt/C film fabricated by drop-casting method; (E), stability results of the 3 MoS_2 films. (Reprinted with permission from Ref. [20], Copyright 2014, Wiley-VCH)

The difference on the releasing sizes of the as-formed hydrogen bubbles is the consequence of constructing different surface architectures. As shown in Figure 3A-C, the flat film that possesses the highest adhesion force shows the biggest releasing size of the gas product (~500 μm in diameter), while the microstructured film can reduce the diameter to ~300 μm. It is found that the releasing size of gas bubbles on nanostructured surface is as small as 50-100 μm, demonstrating the effectiveness of nano-engineering for reducing the solid-gas interaction. The reduced gas bubble size would give rise to the in-time leaving of the adhered gas bubbles and thus diminishes the negative effects (blocking electrolyte penetration and covering working area). As a result, the nanostructured film shows the fastest hydrogen evolution current density increase and the most stable working state (Figure 3D and E). Specifically, for the flat and the nanostructured films, their electrochemical surface areas (can be correlated to the active sites density), Tafel slopes, exchange current densities and series resistances are very close, thus the different current density increase can only be correlated to the different bubble evolution behaviors.

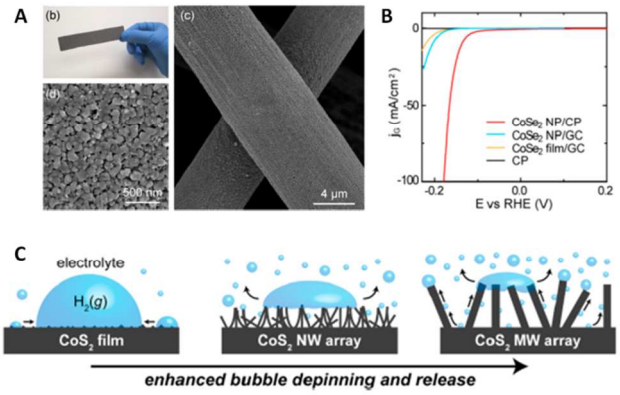

Figure 4. (A) and (B), surface characterizations and HER performance of $CoSe_2$ nanostructured film, (Reprinted with permission from Ref. [33], Copyright 2014, ACS); (C), schematic illustration of the evolution behavior of as-formed gas bubbles on CoS_2 films with different surface structures. (Reprinted with permission from Ref. [35], Copyright 2014, ACS)

This effect can also be expanded successfully to other electro-catalysts for HER. Kong et al. have firstly identified a highly-efficient catalyst of $CoSe_2$ with comparable performance to Pt[23], and further they developed a method to grow a $CoSe_2$ nanoparticulate film (Figure 4A) on a curved substrate to form a three-dimensional electrode, which could deliver a high HER current density at low overpotential and a stable state over a long period (Figure 4B)[45]. Faber et al. also demonstrated the enhanced bubble-releasing effect by constructing three different metallic CoS_2 films (flat, microwire and nanowire film) and comparing their HER performences (Figure 4C).[35]

3.2 Oxygen evolution reaction (OER)

Besides HER, OER is another important component of overall water splitting reaction. Since four electrons are involved to form one molecular of oxygen, this reaction possesses a more sluggish kinetic relative to the HER, thus more efficient catalysts are required to overcome the high reaction barrier.[46] Noble metal oxides (IrO_2 and RuO_2) are the best catalysts for water oxidation, but their scarcities greatly restricted their large-scale application.[47] Alternatively, since nickel and cobalt are identified to be the active center for OER, nickel and cobalt based materials (e.g. mixed transition metal oxides/hydroxides[48-59], cobalt-based perovskites[60, 61] and cobalt phosphates[62, 63]) are demonstrated with comparable OER activities. Recently, carbon based metal free catalysts are also investigated with high OER activity.[64, 65] Similarly, building oriented nanostructures is an effective approach to further improve the overall performance.

Li et al. found that incorporating nickel into cobalt oxides nanowire arrays could increase the surface roughness and thereby enhance the OER performance[66], which is also observed by Lu et al[67]. Our group also demonstrated that combining the intrinsically active electro-catalysts (NiFe-LDHs and Zn-doped cobalt oxides) with appropriate morphologies (nanoarrays[68] and hierarchical nanoarrays[69]) would readily achieve high OER current densities with low overpotentials. This ultrahigh performance was also partially attributed to the low adhesion force of the electrodes to gas products, as demonstrated in the study of hierarchical NiCoFe-LDH nanoarrays[70]. Although the hierarchical nanoarrays did not show a great improvement for further reducing the adhesion force compared with the nanoarrays, the higher porosity and active sites density endowed the electrode with a marginal enhancement for the overall performance. The aforementioned works indicate the performance of OER electrodes can also be benefited by constructing nanoarrays or hierarchical nanoarrays.

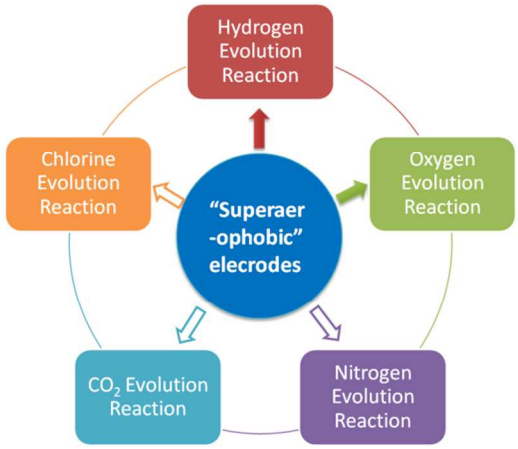

Figure 5. The usages of the low adhesion electrodes. The usages directed by solid arrows have been demonstrated and the usages directed by hollow arrows need to be further explored.

4. Summary and outlook

In this review, several recent works on engineering surface structures of electro-catalysts for GERs are summarized. Besides the high porosity and enhanced conductivity, the nanoarrays and hierarchical nanoarrays can effectively alleviated the adhesion to the gas bubbles, thus affording a fast gas releasing behavior,

resulting in a fast current increase and stable working state. This effect has been successfully applied in several non-noble electrocatalysts for both HER and OER, demonstrating the general efficacy of this concept.

Accordingly, as the noble metal catalysts (Pt, IrO_2 and RuO_2) show the highest intrinsic activities to the corresponding GERs, it is highly expected that ultrahigh performances would be achieved if these catalysts are built into oriented nanoarrays or hierarchical nanoarrays. In addition, since the catalysis reactions only occur at the surface, the noble catalysts can be deposited on the as-prepared conductive nanoarrays or hierarchical nanoarrays to reduce the amount of noble elements without the compromise of the catalytic performances.

Besides HER and OER, this approach should also be valid for other GERs (e.g. methanol oxidation, hydrazine oxidation and chlorine evolution reactions, figure 5) which are essential in national economy but suffer from severe adhesion of the gas products (CO_2, N_2 and Cl_2). It is well known that methanol oxidation and hydrazine oxidation both are important anodic reactions in direct liquid fuel cells and also suffer from severe bubble adhesion problem.[71, 72] Therefore, in the near future, progresses on engineering the catalyst materials for these reactions should be required to circumvent the bubble adhesion problem and substantially improve the GERs performances.

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