Janus electrode with simultaneous management on gas and liquid transport for boosting oxygen reduction reaction

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ABSTRACT

Oxygen reduction efficiency holds the key for renewable energy technologies including fuel cells and metal-air batteries, which involves coupling diffusion-reaction-conduction processes at the interface of catalyst/electrolyte, and thus rational electrode design facilitating mass transportation stands as a key issue for fast oxygen reduction reaction (ORR). Herein, we report a Janus electrode with asymmetric wettability prepared by partly modifying aerophobic nitrogen doped carbon nanotube arrays with polytetrafluoroethylene (PTFE) as a high performance catalytic electrode for ORR. The Janus electrode with opposite wettability on adjacent sides maintains stable gas reservoir in the aerophilic side while shortening O₂ pathway to catalysts in the aerophobic side, resulting in superior ORR performance (22.5 mA/cm² @ 0.5 V) than merely aerophobic or aerophilic electrodes. The Janus electrode endows catalytic performance even comparable to commercial Pt/C in the alkaline electrolyte, exploiting a previously unrecognized opportunity that guides electrode design for the gas-consumption electrocatalysis.

KEYWORDS

Janus materials, electrode, gas diffusion, oxygen reduction reaction, fuel cells

1 Introduction

The oxygen reduction reaction (ORR), serving as the cathode reaction of many electrochemical technologies including fuel cell [1–4] and metal-air battery [5–8], is essential to improve the energy conversion efficiency. To date, numerous efforts have been focused on pursuing advanced catalysts with excellent ORR activities, including Pt-based nanocatalysts [9–14], metal/metal oxides-carbon hybrid materials [15–20] and metal-free catalysts [21–24]. However, little attention has been paid on how to design electrodes with better mass transportation, which is in fact of equal importance for fast oxygen reduction kinetics. In ORR catalysis, limited solubility and sluggish oxygen transport in the solution could not provide enough oxygen sources to the aerophobic/hydrophilic catalyst surface (Figs. 1(a) and 1(d)), resulting in a limited performance of the ORR process happening mostly at the catalyst/electrolyte interface with only the dissolved oxygen [5, 25, 26].

Traditionally, the gas diffusion layer (GDL) for metal-air batteries made by a mixture of polytetrafluoroethylene (PTFE) and conducting carbon was added between catalysts and substrate to handle the low diffusion of O₂ in solution but hindered the electron conductivity from the substrate to the catalysts [27–30]. To address above dilemma between electron conductivity and O₂ transport, we previously grew N-doped carbon nanotubes (N-CNTs) arrays on carbon fiber paper (CFP) and modified them with PTFE to superaerophilic/superhydrophobic to provide sufficient O₂ and keep electron transport

highway at the same time. Of making an integrated gas film underwater, the superaerophilic (SAI) electrodes has demonstrated their fast current increase in 6 M KOH solution [31]. However, the SAI surface might exclude electrolyte infiltration and thus block the ion-diffusion pathway, leading to reduced exposure of the N-CNTs catalysts in the electrolyte and thus minimal utilization of the catalysts (Figs. 1(b) and 1(e)). Noteworthy, the liquid/gas/solid interface is of great importance to ORR, in which the ionically conducting phase, the gas transport phase, and solid catalysts phase combining together as three phase boundary to guarantee the charge transfer reaction proceed efficiently. Therefore, how to design and engineer a rational electrode for accelerating oxygen diffusion and improving ionic/electronic conductivity becomes a key issue in achieving high efficiency of ORR catalysis.

Janus materials with opposite wetting properties [32–34] on different sides have attracted worldwide interests for their possible applications including water collection [35], gas purification [36], and microfluidics systems [37]. It also gives inspiration for ORR electrode design with adjacent aerophilic and aerophobic sides, as shown in Figs. 1(c) and 1(f). For the Janus electrode, the aerophobic side (the blue part in Fig. 1(c)) could be easily wetted by the electrolyte to provide efficient ionic transportation, while the aerophilic side (the yellow part in Fig. 1(c)) could serve as gas collector and transporter as shown in the Fig. 1(d), which provide a good chance to balance gas and ion transportation.

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Figure 1 Schematic illustration of ORR catalyst electrode with different wettability. (a) The hydrophilic catalyst coating on current collector immerses under electrolyte, in which the oxygen diffusion pathway is blocked and (d) limited gas/solid/liquid interface can be created for ORR. (b) and (e) The aerophilic structured electrode where gas film formed outside the catalysts, which accelerate O_2 transport but prevent electrolyte from permeating into the catalysts, resulting in inferior ORR performance. (c) and (f) The Janus electrode has hydrophilic region for electrolyte infiltration and OH^- ions transportation, alongside with aerophilic region for O_2 reserve and diffusion which can provide O_2 reactant for ORR reaction in the hydrophilic region.

Herein, a series of Janus electrodes with asymmetric wettability is fabricated by single-side modification and used as high efficient ORR catalysts. The Janus electrodes were made based on N-CNTs grown on the CFP, followed by modifying single-side with PTFE solution via a finely-tuned finite-depth capillarity deposition process. The PTFE modification imparts the modified side with aerophilicity (hydrophobicity), while the other side without PTFE coating preserves its original aerophobicity (hydrophilicity). In the electrocatalytic ORR, the aerophilic side maintains steady gas reservoir to guarantee sufficient O_2 supply, while the aerophobic side provides sufficient pathway for electrolyte percolation, thus the catalysts in the aerophobic side could get O_2 with shortening diffusion distance from aerophilic side than the external gas supply as well as sufficient electrolyte contacting. The optimized Janus electrode exhibits superior ORR activity with a potential of 0.5 V to reach current density of 22.5 mA/cm^2 compared to merely superaerophilic (11.2 mA/cm^2 @ 0.5 V) or superaerophobic (3.3 mA/cm^2 @ 0.5 V) electrodes, which have the shortage in either ion or oxygen supply. Such Janus electrodes fully demonstrated their advantages of gas and liquid management to boost ORR, and should also shed light on electrode design for other gas-consumption reactions.

2 Experimental

2.1 Synthesis of Co(OH)_2 nanosheet arrays/CFP

The Co(OH)_2 nanosheet arrays were constructed on macroporous carbon fiber paper (CFP) by a solvothermal method. In a typical procedure, $\text{Co(NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1 mmol) and $\text{CO(NH}_2)_2$ (10 mmol) were dissolved in 36 mL of methanol to form a transparent solution by continuous stirring. CFP substrate was pre-treated by ultrasonication in methanol for 10 min, and then the substrate and the as-obtained solution were transferred to a 40 mL Teflon-lined stainless-steel autoclave, which was sealed and maintained at 120°C for 12 h. The Co(OH)_2 nanosheet arrays on CFP were obtained and subsequently rinsed with distilled water and ethanol each for 5 min with the assistance of ultrasonication, and dried at 80°C for 6 h.

2.2 Synthesis of aerophobic N-doped CNTs arrays/CFP

The Co(OH)_2 nanosheet arrays were propped on a porcelain boat which was filled with melamine powder ($\sim 1.4 \text{ g}$) and the porcelain boat was put into the tube furnace with Ar gas flowing. The tube

furnace was heated up to 650°C at a speed of 10°C/min and then held for 30 min to carbonize the melamine and *in situ* grow the nitrogen-doped CNTs on CFP, also named the aerophobic (SAO) film. The mass-loading of N-CNTs was measured as 2 mg/cm^2 .

2.3 Synthesis of Janus N-doped CNTs arrays/CFP

The as-prepared N-doped CNTs was set on $10 \mu\text{L}$ PTFE solution (1 wt.%) which was spread on a flat glass, thus only a thin bottom portion of the N-CNT-CFP was wetted by PTFE solution due to capillary force. The electrode film was dried at 80°C for 15 s after each modification, and the modification cycle numbers were controlled to obtain a series of Janus films, namely, Janus-5, Janus-10, and Janus-15. Subsequently, the Janus films were heated at 350°C for 30 min in Ar atmosphere.

2.4 Synthesis of aerophilic N-doped CNTs arrays/CFP

The N-doped CNTs was soaked in $160 \mu\text{L}$ of PTFE solution (1 wt.%) for 5 min, and then heated at 350°C for 30 min in Ar atmosphere to obtain the aerophilic film (SAI).

2.5 Materials characterization

The structural information of the sample was characterized using a field-emission SEM (Zeiss SUPRA 55) operating at 20 kV and a high-resolution TEM system (JEOL 2100) operating at 200 kV. XPS spectrum was carried out by using a model of ESCALAB 250. X-ray powder diffraction patterns were recorded on an X-ray diffraction (Rigaku D/max 2500) at a scan rate of $10^\circ/\text{min}$.

2.6 Electrochemical measurements

The electrochemical measurements were carried out at room temperature in a three-electrode glass cell connected to an electrochemical workstation (CHI 660D, Chenhua, Shanghai). Saturated calomel electrode (SCE) was used as the reference electrode, and Pt was used as the counter electrode. During all the measurements, O_2 was bubbled at a speed of 30 mL/min to supply O_2 reactant. Cyclic voltammetry was firstly conducted for tens of scans to reach a relatively stable state, and linear sweep voltammetry (polarization curve) with scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$ was measured in KOH electrolytes ($0.1 \text{ mol}\cdot\text{L}^{-1}$). The potential was calibrated with respect to RHE by experimental measurements using two Pt electrodes as working and counter electrodes in the hydrogen-saturated solution. The stability tests of the electrodes were operated at 0.3, 0.35 and 0.45 V vs. RHE for SAO, Janus-10, and SAI electrodes, respectively.

2.7 Wettability characterizations

The liquid droplet and bubble underwater contact angles were measured using a contact angle system (OCA 21, Dataphysics, Germany) at ambient temperature, with the probe liquid ($2 \mu\text{L}$) and oxygen bubble ($2 \mu\text{L}$). The adhesive forces between the oxygen bubbles and electrode interfaces can be assessed by a high-sensitivity micro-electromechanical balance system (Dataphysics DCAT11, Germany).

3 Results and discussion

Fabrication of Janus film was schematically illustrated in Fig. 2(a). Firstly, Co(OH)_2 nanosheet arrays were constructed on the CFP (Fig. S1 in the Electronic Supplementary Material (ESM)) by a solvothermal method as previously reported [26]. Subsequently, the superhydrophilic (i.e., superaerophobic) N-CNTs were *in situ* grown using the Co(OH)_2 nanosheets as the pre-catalyst while melamine as the nitrogen and carbon sources under 650°C . After carbonization, the CFP substrate was densely covered by superhydrophilic N-CNTs arrays (N-CNT-CFP) other than vertical Co(OH)_2 nanosheet arrays, as shown in Figs. S2(a), S3 in the ESM and Movie ESM1, named as

Figure 2 Fabrication of Janus electrodes. (a) Schematic illustration for fabrication of a series of Janus electrodes which starts from N-CNTs arrays with aerophobic (AO) property to different contents of aerophilic (AI) parts by PTFE modification. In which, yellow and blue net represent CNTs arrays with and without PTFE modification. The asymmetric liquid droplet behaviour measurements on both sides of Janus films with (b) 5, (c) 10 and (d) 15 cycles of PTFE modification.

superaerophobic (SAO) electrode. Then, a series of Janus films with different “aerophilic depth” was fabricated by a finely-tuned finite-depth capillarity PTFE deposition process. In practical, as we tested, 160 μL of PTFE solution is enough to fully saturate the whole N-CNTs arrays ($\sim 2 \times 3 \text{ cm}^2$ and 0.28 mm in thickness). Instead of completely soaking, we used PTFE solution with much less volume (e.g., 10 μL) to modify one side of N-CNT-CFP, by lying the N-CNT-CFP on very shallow PTFE solution (10 μL), thus only a thin bottom portion of the N-CNT-CFP was wetted by PTFE solution due to capillary force. The electrode film was dried at 80 $^{\circ}\text{C}$ for 15 s after each modification, and such modification (controlled PTFE capillary deposition) cycles were repeated to increase the PTFE coating portions at the N-CNT-CFP. Then the as-prepared films with different PTFE modification portions were heated at 350 $^{\circ}\text{C}$ in the Ar atmosphere for 30 min to obtain a series of Janus electrodes. Scanning electron microscopy (SEM) images of the N-CNTs before (Fig. S2(a) in the ESM) and after PTFE modification (Fig. S2(b) in the

ESM) illustrated the extension membranes on the N-CNTs (indicated by arrows inset the Fig. S2(b) in the ESM), confirming successful PTFE modification on the coating side.

The electrodes with 5, 10, and 15 cycles of FTFE modification were named as Janus-5, -10 and -15 electrodes, respectively (Fig. 2). The aerophobic sides (blue parts) are noted as “AO” sides and the aerophilic sides (yellow parts) are named as “AI” sides thereafter. The wettability tests were conducted using liquid and gas contact angle measurement to evaluate the changes of wettability for a series of Janus electrodes. As the PTFE modification numbers increased, the hydrophilicity decreased (Fig. 2, AI side) while the aerophilicity increased (Fig. S4 in the ESM). This was demonstrated by the bubble contact angle decrease from 44.1 $^{\circ}$ to 13.4 $^{\circ}$ (the top section of Figs. S4(a)–S4(c) in the ESM), which is more obviously for the AO side: the bubbles converting from “high angle pinning states” (the lower sections of Fig. S4(a) in the ESM) to “penetration states” (the gas bubbles penetrate through the electrodes from the AO side to the AI side when the AO layer was thin enough, like Janus-10 or -15). For Janus-10, the penetration happens occasionally and slowly (255 s, Movie ESM2); but for Janus-15, the AO side is too thin and the AO zones are too small to keep a continual liquid layer, so it happens everywhere and very fast (40 ms, Movie ESM3). Obviously, the ratio of AI portion of the Janus electrodes increased with the increasing of PTFE deposition cycles.

The bubble behaviours on Janus-10 electrodes were further measured in KOH solution. As shown in Fig. 3, the PTFE modified side (AI side) of Janus-10 electrode (the yellow side in Fig. 3(a)) showed small gas bubble contact angle ($22.9 \pm 2.3^{\circ}$, Fig. 3(b)), and large gas bubble adhesion force (114.4 μN , Fig. 3(c)). The apparently “white” surface was due to strong light reflection from continual gas film coating on the AI side underwater (Fig. 3(d)). In contrast, the AO side of Janus-10 electrode (blue colour in Fig. 3(e)) exhibited aerophobic property, demonstrated by quick bubble penetration behaviour from AO to AI side (Fig. 3(f)), weak interaction with gas bubble ($< 10 \mu\text{N}$, Fig. 3(g)) and strong water spreading/dispersion ability (Fig. 2(c) and Movie ESM4), still maintaining the original aerophobicity of as-prepared N-CNTs (Movie ESM1). Also, the dark colour of AO side showed little light reflection, suggesting the well wetting of liquid (i.e., well accessible to electrolytes) into the AO side and excluding the existence of gas film (Fig. 3(h)).

The bubble contacting dynamic of the Janus electrodes was further compared to the SAI electrode with fully PTFE coating and the SAO electrode without PTFE modification. When a bubble touched the AI side of Janus-10, it spread over the AI side and resulted in gas “pinning” state with contact angle of $\sim 22.8^{\circ}$ (Fig. 4(a)). The spreading finished in 32 ms as revealed by a high-speed camera (Fig. 4(a) and Movie ESM5), but the angle changed little and maintained on the AI side in the next 730 ms. The SAI electrode could

Figure 3 The bubble behaviours on both sides of Janus-10 electrode. (a) and (e) Schematic illustration of the gas bubble behaviour on (a) AI and (e) AO side of Janus-10 film. (b) and (f) Gas bubble behaviours on (b) AI and (f) AO sides of Janus-10 electrode. (c) and (g) Adhesion force measurements of O_2 bubbles on (c) AI and (g) AO sides of Janus-10 electrode. Optical photos of (d) AI side and (h) AO side of the Janus film under 0.1 M KOH electrolyte.

Figure 4 2 μL oxygen bubble adhesion behaviours on three different electrodes: (a) AI side of Janus-10, (b) SAI, and (c) SAO electrodes. The oxygen bubble is easily pinned and spread out the AI side of Janus-10 and SAI electrodes under electrolyte, indicating an accelerated oxygen diffusion process. In contrast, bubble rolls away on the SAO electrode. Schematic illustrations of the three phase interface conditions underwater on (d) non-uniform PTFE modified Janus electrode with capillary deposition and (e) SAI electrode with continuous gas film using complete immersion.

also absorb and spread out an O_2 bubble in tens of milliseconds, with an even faster speed than AI side of Janus-10 (Fig. 4(b) and Movie ESM6). The contact angles of bubbles on SAI electrode turned smaller with time extended, which is different from the AI side of Janus-10. Eventually, the bubbles transported crossover the film to the top surface (the red arrows in Fig. 4(b)), driven by buoyancy force along the gas tunnels with PTFE modification. Although the AI side of Janus-10 film could not transport gas across the aerophobic portion because the porous structure of the hydrophilic portion (Fig. S2(a) in the ESM) offering dense water film hindered the gas penetration, the AI side still could collect and reserve gas in time. In contrast, the SAO electrode repulsed bubbles when they contacted the surface, kept the spherical shape and rolled off from the surface with ease (Fig. 4(c) and Movie ESM7), which indicated losing contact

with bubbles and only dissolved O_2 can be used during ORR. The capturing of O_2 improved in Janus electrode, demonstrating the importance of PTFE modification on gathering gas bubbles rapidly underwater.

It should note that there are no obvious structural changes in the Janus electrode although the wettability transfers from aerophobic to aerophilic after PTFE modification. Besides SEM on the two sides of the Janus film (Fig. S2 in the ESM), we further evidenced this point by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy (Fig. S5 in the ESM). This provides the base for wettability effects investigation. Different from previous overwhelming coating of PTFE, the repeated capillary coating led to aerophilicity on one side and leaving the other side still hydrophilic. More importantly, such process created a hydrophilicity gradient along the deposition direction perpendicular to the film, which also caused randomly distributed but cross-linked AO/AI zones at the inside plane parallel to the thin film electrode, similar to the patterns with newly creating edges [33]. The AO/AI zones with aerophilicity gradients at the inside plane should be similar to the AI side of Janus-5 electrode with insufficient PTFE modification, possessing discontinuous gas film underwater (Fig. S6 in the ESM) and inducing a large amount of microgroove gas/solid/liquid interfaces at the AI/AO transitional interface (Fig. 4(d)), much more than that for continuous AI/liquid interface in Fig. 4(e) [25], let alone the AO electrodes. Above results illustrated that the PTFE modified sides of Janus electrode could not only serve as a gas reservoir and shorten the gas transport pathway to AO portions as a good electrolyte/ion transporter, but more importantly, afford more gas/solid/liquid three phase interfaces to serve as reaction zones.

The unique wetting property endows superior catalytic performance of the as-prepared Janus electrode towards ORR, which was demonstrated using a three-electrode system in 0.1 M KOH aqueous electrolyte with continuous bubbling of oxygen (Fig. 5(a)). For comparison, commercial Pt/C, SAO, and SAI electrodes (see Experimental section for details) were also tested. As shown in the polarization curves in Fig. 5(b), the Janus electrode exhibited superior performance with a low onset potential at ~ 0.94 V and rapid current density growth reaching a current density of $22.5 \text{ mA}/\text{cm}^2$ at 0.5 V versus the reversible hydrogen electrode (RHE), superior over SAO

Figure 5 Electrocatalytic performance of Janus, SAI, SAO and commercial Pt/C. (a) Schematic illustration of transport and reaction pathways on the Janus electrodes for ORR. (b) ORR polarization curves of the SAO, Janus-10, SAI, and commercial Pt/C electrodes in the oxygen-bubbled 0.1 M KOH solution without IR-correction, showing the Janus-10 electrode with the fastest current density increase. (c) The ECSA measurements of the three electrodes plotting as a function of scan rate measured at 0.025 V vs. SCE: SAO, Janus and SAI electrodes, alongside with the SAI electrode after 10 h test. (d) ORR polarization curves of the electrodes with various aerophilic thickness in oxygen-bubbled 0.1 M KOH solution without IR-correction, showing the Janus-10 electrode with the best performance. (e) Plots of ECSAs and ORR current densities at 0.5 V vs. RHE for Janus electrodes with different aerophilic thicknesses. (f) Stability results of the three electrodes at a constant overpotential.

and SAI electrodes, and even comparable to that of commercial Pt/C. Detailed comparison of different ORR catalysts is summarized in Table S1 in the ESM. Notably, at low overpotential region (0.8–0.9 V vs. RHE) where the diffusion of O₂ in the electrolyte is not the limiting factor while the dissolved oxygen is the main source for ORR, the current density of SAO electrode was much higher than that of SAI electrode (Fig. 5(b)), illustrating SAI electrode has limited contact area with the electrolyte. Interestingly, Janus electrode showed similar behavior to SAO electrode at low overpotential range but rapid current increase as SAI, which combined the merits in one with balanced wetting property to gas and ions transport (Fig. 5(b)).

The unique ORR activity was further supported by the electrochemically active surface area (ECSA) measurement using electrochemical double layer capacitance (EDLC) as the indicator. EDLC was used to estimate hydrophilic areas of the electrodes [38] because only liquid/solid interface could induce adsorption/desorption of cations and anions with cyclic voltammetry measurement and thus contribute to the double layer capacitance. As expected, SAI electrode only showed 1.2 mF/cm² (Fig. 5(c) and Fig. S7(a) in the ESM), less than 5% of that for SAO electrode (25.9 mF/cm², Fig. 5(c) and Fig. S7(b) in the ESM), which confirmed that liquid was excluded from the catalysts (N-CNTs) inside SAI electrode leading to few electrolyte/catalyst interface and thus negligible current at low overpotential and limited gas/solid/liquid areas (the reaction zones) for further reaction [27, 29]. Noted that the ECSA value for Janus-10 film (10.5 mF/cm², Fig. 5(c) and Fig. S7(c) in the ESM) is approximate 2/5 to that of SAO electrode, revealing AI portion as gas reservoir occupied 3/5 of the whole Janus electrode, and the remaining AO side provided access for catalysts to contact electrolyte and offered much more catalyst/electrolyte interfaces, resulting in fast current increasing rate at applied potential window compared with SAO and SAI electrode. The unique asymmetric property of the electrode indeed played a significant role on the electrocatalytic ORR performance. This could be attributed to the synergistic effect of two sides with opposite wettability and non-uniform modification introducing more gas/solid/liquid interface areas. That is, for the AI side with PTFE modification, O₂ bubbles were captured quickly and then transported to the three phase contact lines (TPCL) with catalyst/electrolyte coexist (Fig. 5(a)) driven by aerophilicity gradient; while the unmodified hydrophilic side provides access to electrolyte and release resultant OH⁻ ions smoothly. On the other hand, capillary deposition from only one side introduced non-uniform wetting areas and jagged aerophobic/aerophilic zones with much more TPCLs (Fig. 4(d)) for ORR [5, 25]. In contrast, SAO electrode with insufficient oxygen supply exhibited limited current density at high overpotential (0.2–0.8 V), owing to low solubility and slow diffusion of O₂ in the electrolyte. For SAI electrode, it showed inferior performance to Janus-10 electrode but superior over SAO electrode, indicating oxygen supply is more critical for ORR efficiency. Though SAI electrode could easily gather O₂ to the electrode surface (Fig. 4(b)) thus guaranteed sufficient reactant gas supply under high overpotential, the dense gas film made electrolyte hardly to permeate inside the SAI electrode, resulting in a limited performance due to the liquid phase is necessary for reaction and resultant OH⁻ ions release. These results illustrated that both gas transport and ion channels are of great importance.

To attain the best ORR performance, Janus electrodes with different AI depths were used as working electrodes for comparison. From polarization curves in Fig. 5(d), the Janus-10 electrode with appropriate thickness and high contrast wettability on adjacent sides with optimized gas transportation as well as ion diffusion exhibited superior ORR performance compared to the other electrodes with slow gas diffusion for Janus-5 and insufficient ion transport for Janus-15. Janus-5 electrode with too thin aerophilic part showed large ECSA (Fig. 5(e) and Figs. S8(a) and S8(b) in the ESM) and too

weak aerophilicity (Fig. 2(b)), therefore could not supply a stable and continuous gas transportation channels and reservoirs. Conversely, Janus-15 with much thicker aerophilic areas than Janus-10 electrode was very similar to SAI, exhibited little hydrophilic areas (Figs. 2(c) and 2(d)), resulting in hardly contact with electrolyte and had shortage of ion-transportation, which was evidenced by small ECSA value in Fig. 5(e) and Figs. S8(c) and S8(d) in the ESM. Above results demonstrated that Janus electrode with proper aerophilic ratio was critical to enhance ORR activity, which could provide continuous and stable gas film serving as a reservoir while the hydrophilic portion ensuring electrolyte access to catalysts.

Long-term stability is a crucial criterion to evaluate the performance of the catalysts. As showed in Fig. 5(f), the chronoamperometric response revealed excellent stability of Janus-10 electrode, with negligible current attenuation even after 18 h tests (black line). For SAO electrode, the working stability is good but only working at very low current (red curve in Fig. 5(f)). Surprisingly, the current density of SAI electrode showed a significant increase (~ 30%) in the first 3 h and remained stable afterward. This was attributed the wetting behaviour change on SAI electrode. SAI endows the electrode with limited ion channels originally, but as ORR extends in time, consumption of oxygen makes electrolyte penetrate into the aerophilic regions, increasing the hydrophilic zones with weaken aerophilicity, which induces more TPCLs and ion channels thus benefits the ORR performance. This point was verified by the increase of ECSA (dotted line in Fig. 5(c)) and reduce of hydrophobicity (Fig. S9 in the ESM) of SAI electrode after chronoamperometric test. In general, the Janus electrode showed excellent working stability owing to the rational design to balance gas and ion transportation during ORR catalysis.

4 Conclusions

Janus electrode with asymmetric wettability was prepared by controlled PTFE capillarity deposition for tailoring ratio of aerophilicity and aerophobicity. On the one hand, the aerophilic parts of Janus electrodes show strong interaction with gas, which is beneficial to O₂ transport overcoming low O₂ solubility and slow diffusion rate in the solution, on the other hand, the aerophobic ones have high capacity for absorbing and maintaining water, providing efficient channels for ion transport. The integration of aerophilic and aerophobic components into one electrode (e.g., Janus) not only captures and keeps stable gas film as O₂ reservoir and shortening the O₂ transport pathway to active sites in gas/solid/liquid interface and hydrophilic catalysts, but also ensures the quick immigration and release of ion. The special Janus electrode exhibited superior ORR activity of ~ 0.94 V onset potential and rapid current growth without current density limitation, superior over merely superaerophilic and superaerophobic electrodes. The success illustrates that constructing a Janus structure with asymmetric wettability is a promising protocol to balance the gas and ion transportation, and improve the performance of energy conversion devices involving gas-consumption reactions.

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Electronic Supplementary Material: Supplementary material (supplementary SEM and TEM images of N-CNTs electrode and its

precursors materials, XPS and Raman spectra, ECSA measurement, wettability performance and bubble behavior on ORR electrodes as well as supplementary Table and Movies) is available in the online version of this article at <https://doi.org/10.1007/s12274-018-2199-1>.

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