Investigation on the variation law of gas liquid solid three phase boundary in porous gas diffusion electrode

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Abstract

The three-phase boundary length will change with the electrochemical reaction in the working process of the gas diffusion electrode. The process of porous media fluid interface movement is investigated by establishing the physical and mathematical model of the microporous electrode. Using a numerical simulation method, the electrode section electron micrographs are topologically gridded to investigate the micro flow phenomenon of the gas diffusion electrode in the zinc-air battery. By simulating the development process of the electrolyte interface in the porous electrode, the law for the variation of the total length of the three-phase boundary is observed. The results show that the total length of the three-phase boundary increases first and then shortens with the change of gas diffusion and electrolyte electrode movement. A similar trend is observed when the peak power is varied. A theoretical expression for that defines the changes in the length of the three-phase boundary is provided. Finally, we show that the topology and the grid method are feasible means that can be used to analyze electrochemical reactions in complex multiphase flows.

Keyword: Electrochemistry
1. Introduction

Gas diffusion electrodes are widely used in different varieties of fuel cells and metal-air electrodes. It is known for its good permeability but at the same time restricts the penetration of liquid. The gas diffusion electrode has a compressed gas transmission channel where the electrolyte forms a thin layer of liquid film on its surface. This region provides favorable conditions for the stable coexistence of gas, liquid and solid [1, 2] which promotes the electro-catalytic reduction of O₂. Currently, activated carbon and other highly conductive materials such as graphite are widely used in zinc-air battery cathodes due to their excellent adsorptive properties [3]. The electrode material is mixed as dense electrode porous structure, which can achieve the good technology affirmative requirements.

The exploration and selection of catalysts in positive electrodes have always been one of the hot topics of researchers [4, 5, 6]. Precious metal catalysts, such as platinum and silver, have been found to have excellent catalytic effects [7]. Similarly, the catalytic activities of their alloys, such as PtCo, PtNi and PtFe, were also found to be higher compared to other common metal alloys [8, 9, 10, 11]. However, due to economic considerations, these metals and their alloys are hardly widely used as catalysts. The transition metal oxide also has a certain degree of oxygen reduction activity especially manganese oxide and cobalt oxide in alkaline conditions showing excellent activity for oxygen reduction [12, 13, 14, 15]. The transition metal oxide has achieved the practical application level while achieving excellent discharge performance and stability and reducing the cost of the catalyst so far widely used. Also, the main material of the gas diffusion electrode, the activated carbon itself has a specific catalytic capacity.

The study of the electrochemical reactions sites in gas diffusion electrodes is important in the understanding of their three-phase boundary [16]. The electrode reaction occurs at the three-phase boundaries (TPBs), where the catalyst, electrolyte, and gas meet and react [17, 18, 19, 20, 21] proposed density of electrochemically active triple phase boundary sites is one of the most critical factors that affect the performance of composite cathodes in solid oxide fuel cells. Only the topologically connected triple phase boundaries can become electrochemically active [22] found that the sintering temperature is also essential for composite electrodes to increase the active triple phase boundary line (TPBL) between electrode, electrolyte and gas phase, leading to a decrease in the polarization resistance with decreasing sintering temperature. The research done by [23] presented a remarkable improvement in the electrochemical performance, through a significant enlargement of the three-phase boundary region by an optimization of the surface structure, in solid oxide fuel cells (SOFCs) [24] also proposed that electrochemical reactions in solid oxide fuel cells take place around three-phase boundaries (TPBs). The electrochemically active zones (EAZs) are generated in three-dimensions around the TPBs of on-running SOFCs [25] constructed a model to investigate the relationship between the overpotential
and the three-phase boundary (TPB) length of the electrodes composited by the porous La$_{0.81}$Sr$_{0.09}$MnO$_3$ and LSM-YSZ of the solid oxide fuel cell. Three-dimensional distribution of TPB for the composite cathode was suggested. The effective thickness was observed to be less than 20 microns [26] also constructed a mathematical model to calculate the volume specific three-phase boundary length in the porous composite electrodes of the solid-oxide fuel cell. The model is exclusively based on geometrical considerations accounting for porosity, particle diameter, particle size distribution, and solids phase distribution. Not only in metal-air cells and fuel cells, but also in other fields, such as sensors, the porous electrode also need the large three-phase boundary [27] presented a theoretical model for quantifying the number of three-phase boundary sites using the impedance spectrum of porous electrodes used in exhaust gas sensors [28] found that the sensor showed excellent stability and speedy response kinetics. He also said that NO$_2$ -sensing properties might be due to the enlargement of the area of the three-phase boundary.

The three-phase boundary is a region where gas, liquid and solid phases co-exist. This is considered as the effective area of electrochemical reaction. It is crucial to define the change law to better understand the nature of the electrode reaction and rational control. Taking the gas diffusion electrode as the research object, the physical and mathematical model of the microporous electrode was established. The law of changes of electrolyte movement with time in the zinc-air battery was explored. The electrolytic movement process was simulated by using the topological grid structure. The calculated values from the proposed mathematical model and the simulation process were compared and analyzed. The experiment comparison of the infiltration of peak power and change of electrode electrolyte in electrode have verified the agreement of the model and the simulation to reveal the change rules of the three-phase boundary in gas diffusion electrode.

2. Materials and methods

2.1. Models

2.1.1. Physical model of microporous seepage

The pore structure of porous medium is extremely complicated. Even if the porosity of two kinds of porous bodies are identical, their respective pore diameters, lengths, positions, directions, section shapes and the hydrophobic characteristics of their pore wall surfaces will still have considerable differences. Therefore, it is necessary to determine the motion of the liquid interface in a given micro-pore when the process of liquid interface in porous media is studied.

As can be seen in Fig. 1a, the diameter of the micro-pore of the gas diffusion electrode is about 1 μm. The shapes of the cross-section of the micro-pore include round
pores, square pores and slits. It is assumed that the cross section is round and that the pore diameters are 1 \( \mu \text{m} \). These assumptions are used in the physical models of liquid interface penetration to approximate the law of fluid interface motion in a micro-pore. The physical model of microporous seepage is also shown in Fig. 1b.

Because the liquid interface moving forward in the pore is mainly driven by the surface tension of the liquid, surface tension can be expressed as [29]:

\[
F = \alpha \cdot 2\pi a \cdot \cos \theta \tag{1}
\]

In the Eq. (1), \( \alpha \) is the coefficient of the surface tension of the liquid, and \( \theta \) is the contact angle, which refers to the inclination angle of the free face inclined wall with the solid wall as the boundary, and \( a \) is the radius of the micropore (shown as the Fig. 1b).

The electrolyte used in the experiment is KOH solution, which is conveniently treated and approximated here as water. The surface tension coefficient of water is based on the empirical equation of Harkins:

\[
\alpha = 75.796 - 0.145t - 0.00024 \, r^2 \tag{2}
\]

In Eq. (2), \( t \) is the Celsius temperature, \( \alpha \) is the surface tension coefficient of water, the unit is \( \text{mN m}^{-1} \). Under the experimental condition of 20 °C, the surface tension coefficient is 72.8 mN m\(^{-1}\).
The possible resistance to penetration is provided by gravity $G$:

$$G = \rho gh \cdot \pi a^2$$  \hfill (3)

In Eq. (3), $h$ is the level of the liquid in the micro-tube, i.e., at most not exceeding the electrode height more than 1 mm. The interfacial driving force $F$ of electrolyte does not change with the increase of liquid level, while the resistance $G$ increases with the increase of liquid level. It is found that when the resistance is at its maximum, that is, when the liquid level is maximum 1 mm, the driving force $F$, and the resistance $G$ are equal when $\theta = 89.998^\circ$. The difference in the contact angle will have a direct effect on the relationship between the driving force $F$ and the resistance $G$, as shown in Table 1.

As shown in Table 1, depending on the contact angle, the relationship between the resistance $G$ and the driving force $F$ can be divided into three cases. When $89.998 < \theta < 180^\circ$, the surface tension is less than gravity, that is $F < G$ or the direction of the surface tension and the gravity is same, and both are the resistance. The infiltration process will not occur at this time, and there is no liquid interface movement in the pores so that the micro-pores can be considered as hydrophobic pores. When $89.981 \leq \theta \leq 89.998^\circ$, the surface tension and gravity are in the same order of magnitude, that is the surface tension of $F$ satisfies $G \leq F \leq 10G$. At this point, the surface tension and gravity should not be ignored. However, the range of the contact angle is minimal, and the actual process of microporous osmosis occurs at a contact angle that is far less than 89.981°. We think that this situation will not happen in reality and so this situation will not be analyzed in depth. When $0 < \theta < 89.981^\circ$, the surface tension of $F$ is far larger than the gravity $G$, in such a way that $10G < F$, and the resistance caused by gravity is negligible. In fact, the contact angle in the micro-pore of the infiltration process is mostly located within this region. On the other hand, without considering gravity, differences between the level micro-pore and the vertical micro-pore is negligible, so the micro-pores in the gas diffusion electrode can be treated in the same way, which can bring great convenience to the analysis of the phenomena and the study of the experiments. Therefore, the theoretical analysis of the physical model will not focus on the influence of gravity on the liquid propulsion.

| $0 < \theta < 89.981^\circ$ | $89.981^\circ \leq \theta \leq 89.998^\circ$ | $89.998^\circ < \theta < 180^\circ$ |
|---------------------------|---------------------------------|---------------------------|
| $F >> G$                  | $F$ and $G$ are in the same order of magnitude | The resultant force of $F$ and $G$ is resistance |

Table 1. The influence of contact angle on the relationship between the surface tension $F$ and the resistance $G$ with pore aperture 1 $\mu$m.
On the other hand, the pore size also has some influence on the relationship between the driving force $F$ and the resistance $G$.

For instance, as shown in Fig. 1, when the maximum aperture is 10 $\mu$m, the resistance is at its maximum, i.e., the liquid surface height takes the maximum level of 1 mm. At this point, when $\theta = 89.981^\circ$, the driving force $F$ is equal to the resistance $G$. The influence of the difference of the contact angle on the size of the driving force $F$ and the resistance $G$ is shown in Table 2 for this aperture size.

As shown in Tables 1 and 2, the results assume that the height of the liquid level is obtained by the maximum value. However, in reality, when the liquid in the gas diffusion electrode is still in its unsteady stage, the interface has not yet reached the highest value, the calculated critical value will be larger. That is to say, when the contact angle satisfies $0 < \theta < 89.807^\circ$, the unsteady and steady state of the liquid interface motion can ignore the influence of gravity on the liquid interface motion.

To sum up, the contact angle and aperture size will influence the order of magnitude relationship between driving force $F$ and resistance $G$ in the process of pore penetration. The contact angle plays an essential role in microscale. Within the scale scope of the porous electrodes, the aperture size on the size of the order of magnitude relationship between driving force $F$ and resistance $G$ of the critical value has some influence, but not significantly. Under the experimental conditions, we divided the micro-pore of the porous gas diffusive electrode into two species:

I. No liquid hydrophobic pore, corresponding to the resultant force of driving force $F$ and resistance $G$ as a resistance.

II. The driving force $F$ is much larger than the resistance $G$, making the pores apparently hydrophilic and easily permits the penetration of the liquid. The influence of gravity on the interface motion is neglected in such cases.

In this section, the physical model of micro-pore seepage is required to meet some preconditions: micro-tube sections should have the same shape; the lower liquid source should be infinitely larger than that of the micro-pore aperture, there should be no restriction to the flow, and that the characteristics of hydrophobic water on the surface of micro-pore tubes wall should be consistent.

### Table 2. The influence of contact angle on the relationship between the driving force $F$ and the resistance $G$ with pore aperture 10 $\mu$m.

| $0 < \theta < 89.807^\circ$ | $89.807^\circ \leq \theta \leq 89.981^\circ$ | $89.981^\circ < \theta < 180^\circ$ |
|-----------------------------|------------------------------------------|---------------------------------|
| $F >> G$                    | F and G are in the same order of magnitude | The resultant force of $F$ and $G$ is resistance |

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2.1.2. Mathematical models of microporous seepage

The governing equations for the incompressible flow of homogeneous fluids, namely the mass and momentum conservation equations, are written as [29]:

\[ \nabla \cdot \mathbf{v} = 0, \quad \frac{d\mathbf{v}}{dt} = \frac{1}{\rho} \nabla p + \mu \nabla^2 \mathbf{v} \]  

(4)

Since the velocity and the change rate of the velocity of liquid in pores are very small, the motion of the liquid interface can be approximately considered as a quasi-static process. All the fluid particles in the physical model are assumed to move along the axial direction in the micro-tube, so the flow can be treated as a constant parallel shear flow.

Now, taking a cylindrical coordinate system \((x,r,\phi)\) as shown in Fig. 1b, which makes the X-axis coinciding with the micro-tube axis, where the positive direction points to the air side of the gas-liquid interface. According to Eq. (4), the velocity component can be expressed as

\[ v_x = v(r), \quad v_r = v_\phi = 0. \]  

(5)

Then, it is assumed that the pressure difference caused by the capillary force is uniformly distributed along the micropore section, and the radial pressure gradient is constant. Combining Eqs. (4) and (5), this is formally written as [29]:

\[ \frac{\partial p}{\partial r} = \frac{\partial p}{\partial \phi} = 0, \quad \frac{dp}{dx} = \frac{\alpha \cdot 2 \pi a \cdot \cos \theta}{\pi a^2 \cdot h}. \]  

(6)

Basing on Eq. (6), the momentum relation of the liquid in the micro-pore will satisfy Eq. (7) when it is converted into cylindrical coordinates [29]:

\[ \frac{1}{r} \frac{d}{dr} \left( r \frac{dv}{dr} \right) = -\frac{1}{\mu} \frac{\alpha \cdot 2 \pi a \cdot \cos \theta}{\pi a^2 \cdot h} \]  

(7)

The boundary condition satisfies the non-slip on the pipe wall, and the velocity on the pipe axis remains bounded:

\[ r = a, \quad v = 0; \quad r = 0, \quad v < \infty, \]  

(8)

and can be obtained by solving the following formula:

\[ v(r) = \frac{\alpha \cdot \cos \theta}{2 \mu ah} (a^2 - r^2) \]  

(9)

Since the change of velocity in the porous surface along the radial direction is not as significant as the average speed of the liquid movement in the micro-pore. We need
to obtain the integral pipe flow flux after getting the velocity distribution basing on Eqs. (8) and (9) [29].

\[ Q = \int_{0}^{a} v(r)2\pi r dr = \frac{\pi \alpha \cdot \cos \theta}{4\mu h} a^3 \]  

(10)

So, according to Eq. (10), the average speed is

\[ \overline{v} = \frac{Q}{\pi a^2} = \frac{dh}{dt} = \frac{\alpha \cdot \cos \theta}{4\mu h} \]  

(11)

From Eq. (11), it can be seen that the average speed of the liquid level is a function of liquid surface altitude \( h \). The corresponding relationship between the position of the interface and time can be obtained by integrating the differential equation above:

\[ h(t) = \sqrt{\frac{\alpha \cdot \cos \theta}{2\mu} t + C} \]  

(12)

In Eq. (12), from the initial condition \( h(0) = 0 \), the final form of the interface position changing with time is obtained

\[ h(t) = \sqrt{\frac{\alpha \cdot \cos \theta}{2\mu} t} \]  

(13)

The following three points can be surmised from Eq. (13):

I. In a given micro-pore, the leaching amount of \( h \) is in the second function of the axis of symmetry along the \( y \)-axis with time \( t \), and the initial growth of leaching is fast, while the latter is slow;

II. Under the same conditions, the smaller the diameter of the micro-pore tube, the slower the immersion process, and the larger pore will be quickly filled with liquid;

III. The specific value of the contact angle has a straightforward influence on the leaching amount \( h \), especially when the \( \theta \) is approaching 90°, and the immersion time has an influence on the order of magnitude.

2.2. Experimental

2.2.1. Making the gas diffusion electrode

The electrode used in this experiment is a double layer carbon electrode. The reaction layer is near the electrolyte which is the main site of electrochemical reaction in the gas diffusion electrode. The air layer is close to the air side, which has the function of separating water and allowing air to pass through. The foam nickel skeleton
used in the experiment has height and width of 100 mm by 100 mm respectively, supporting and conducting the electrode. The reaction layer coating is a mixture of PA-1 activated carbon powder, F-2 graphite and acetylene black with a mass ratio of 8:1:1. uniform mixture, air layer coating by acetylene black and the amount of PTFE(Polytetrafluoroethylene) emulsion uniform mixture, adding ethanol to two kinds of coatings with stirring, after the adjustment to the colloidal state, the porosity of the coating into the foam nickel skeleton. The two layers of gas diffusion electrodes are then put into the oven to be heated in the constant temperature 325 °C for ten minutes to make the PTFE emulsion in the air layer be made into a membrane. The ethanol in the electrode is volatilized at the same time. Through the treatment mentioned above, the air layer develops good hydrophobic characteristics [30]. Finally, two layers of gas diffusion electrodes are welded together with 5 mm wide nickel strips, so the effective discharge area of the final gas diffusion electrode is 90 mm * 90 mm.

2.2.2. Experiment design

The zinc gel used as a cathode in the experiment is made from the electrolytic zinc powder of IBC-4 mixed with sodium polyacrylate and distilled water. Sodium polyacrylate powder and the distilled water were mixed to be a viscous liquid with a mass fraction of 1%. The mixture was thoroughly stirred and adequately heated to accelerate dissolution. When there is no clear block, and viscous liquid is obtained entirely by dissolving, the zinc powder that is two times quality than viscous liquid was added to the liquid. After thoroughly stirring the zinc powder and the sodium polyacrylate viscous solution without any further stratification or precipitation, the zinc gel can finally be used.

The electrolyte used in the experiment was potassium hydroxide solution with a mass fraction of 33 %.

The gas diffusion electrode needs to be easily removed from the battery because the immersion liquid amount of the gas diffusion electrode needs to be measured. A schematic diagram of the experimental device is shown in Fig. 2. From bottom to top, it is composed of the zinc gel, diaphragm paper, and a double layer of gas diffusion electrode effectively composed of an air layer and a reaction layer. First, enough

![Fig. 2. Schematic diagram of discharge structure of the gas diffusion electrode immersion liquid test.](https://doi.org/10.1016/j.heliyon.2018.e00729)
zinc gel is poured into the experimental framework, and is then slowly injected with the electrolyte. The electrolyte is filled between the zinc particles until it completely covers the zinc gel. A diaphragm paper is spread over the zinc gel effectively putting it right below the gas diffusion electrode. In the gas diffusion electrode, the reaction layer is below, close to the electrolyte liquid boundary, and the air layer is on top close to the air gas boundary. The electrolyte is dipped into the gas diffusion electrode from the bottom up.

First of all, zinc gel used in the experiments had adequate zinc powder particles, and each discharge performance test requires only a few minutes during which small amounts of ZnO are generated. Their influence on the working performance of zinc electrode can be ignored. The resistivity of zinc, which is the main material of zinc electrode side, is about $5.20 \times 10^{-8} \ \Omega \ \text{m}$ while the resistivity of the gas diffusion electrode, which is made up of graphite, is about $8 \times 10^{-6} \ \Omega \ \text{m}$. This means that the resistivity of the zinc electrode in the battery is lower than the gas diffusion electrode by two orders of magnitude. Basing on the two aforementioned reasons, it can be concluded that the discharge performance of the gas diffusion electrode directly determines the overall discharge performance of the battery under the precondition of sufficient zinc content. Therefore, the overall voltage and current curve of the battery can be used as a physical quantity to measure the discharge performance of the gas diffusion electrode.

The double gas diffusion electrode is covered above the sponge with diaphragm paper and full of electrolyte for storage and immersion to avoid self-discharge, electroosmosis or other factors that may affect the anode discharge performance and immersion process. For the gas diffusion electrode, the liquid boundary is wholly infiltrated diaphragm paper by the electrolyte, and there is plenty of electrolyte source supply in the electrode process, that is, the liquid boundary conditions of the gas diffusion electrode are same. Therefore, the above method can be used to simulate the immersion process of the gas diffusion electrode in the actual battery when it does not discharge.

The pore structure of gas diffusion electrode is complex, and it is difficult to experimentally observe the immersion process and liquid level distribution. However, the quality of infusion will obviously change along with the electrolyte during the immersion process and is easy to measure. The quality through measuring immersion can reflect the different stages of the electrolyte leaching into the gas diffusion electrode.

The immersion amount of gas diffusion electrode is obtained by measuring the weight gain of the electrode. The gas diffusion electrode on the diaphragm paper is moved and placed on a digital balance to be weighed. The gas diffusion electrode will be adhered to a layer of thin liquid film on the surface after pulling away from the diaphragm paper, which is not involved in the liquid infiltration process in porous media, so it is necessary that the quality of the thin liquid film be subtracted.
from the total weight gain. We define $m_1$ as the weight of the dry gas diffusion electrode. The gas diffusion electrode was pulled away quickly after contacting the diaphragm paper, at which time the liquid immersion process has not yet started. The measure weight at this stage is defined as $m_2$. $M_2 - m_1$ is the quality of the thin liquid film on the surface of the reaction layer. After several measurements, the mass of the liquid film on the surface of reaction layer was approximated to be within 0.57 g ± 0.05 g. The error of the measured weight is within 9%. This shows that the measurement method is feasible since the error is within the allowable range. So, the mass of the electrode measured is more substantial than that of $m_2$ is the mass of the liquid immersing in the porous gas diffusion electrode.

It can be seen from Eq. (13) that the permeation process of electrolyte in the gas diffusion electrode micro-pore is prolonged, and the rate of leaching decreases over time. Therefore, it is necessary to have some specific time intervals between the measured time points of immersion and the discharge performance. In the early stage of the immersion, the data collection points need to be more intensive and the measurement time interval needs to be shorter.

The selected experimental time intervals were set at the beginning of immersion, 2 hours, 6 hours, 24 hours, 48 hours, 72 hours, and 96 hours. The current-voltage values were measured by the current adjustable constant transport electrometer and voltmeter.

### 2.3. Simulation

It is experimentally difficult to observe the mesoscopic physical and chemical process of the porous gas diffusion electrode, including the electrolyte interface movement and the change rules of the three-phase boundary length. For this purpose, numerical simulation methods [31, 32, 33] can be used [34] to study the mesoscopic percolation of the gas diffusion electrode. By simulating the development process of the electrolyte interface in the porous electrode, the change rules of three phase boundary length can be observed.

Fig. 1a shows a general view of a gas diffusion electrode with a micropore distribution and a microporous morphology. For this reason, it is chosen as an example to simulate the propulsion of a liquid interface in a gas diffusion electrode. Fig. 3 further illustrates the pore structure and physical significance shown in each region of Fig. 1a. In Fig. 3, once can see ① two large aperture porosity areas, ② dense regions of pore distribution containing a large number of pores, ③ a hydrophobic area of PTFE emulsion ④ cross section of the foam nickel skeleton. The micro-pores can be divided into three kinds according to pore size: large pores with apertures greater than 4 μm, middle pores with apertures about 2 μm and small pores with apertures less than 1 μm. According to the classification rules, the electrode part shown in Fig. 3 is transformed into a topology grid model shown in Fig. 4.
**Fig. 3.** Diagram of the area division of electron microscopy image of the electrode ① macropore ② main pore area ③ drainage area ④ nickel foam skeleton.

**Fig. 4.** Topological network model of the transformation of electron microscopy image of gas diffusion electrode.
As shown in Fig. 4, there is a $44 \times 30$ grid, grid intersections represent nodes, and grid lines represent the microporous pipe, each node has four microporous pipes. The area shown in Fig. 1a were averagely divided into the grid of Fig. 4; the grid is a four channel model; each pore length is 5 μm.

The grid lines of three kinds of colors represent three kinds of micro-pore, which were manually set up by contrasting electron microscopy photographs before the simulation. Among them, the red grid represented the hydrophobic tube wall of micro-pore or small diameter pore. These pores are hardly liquid or need a long time to permeate, which were unified as void micro-pore. The blue grid represented hydrophilic mesopores, and the penetration rate is slow. The green grid represented hydrophilic macropores, and the penetration rate is fast. Then, the ratio of penetration time for mesopore and macropore is 2:1 as calculated from Eq. (13), and then the time were converted to the time steps for simulating penetrating through each pipe. We can get the liquid interface movement and the permeability distribution of micropore after a certain number of time steps.

3. Results and discussion

3.1. Peak discharge power curve of gas diffusion electrode under different immersion charges

Fig. 5 shows the peak discharge power curve of gas diffusion electrode under different immersion charges. When liquid starts to immerse, and the immersion charge is on a low level, electrode’s peak discharge power had a small promotion, after that, it declined as the increase of the immersion. Peak discharge power, to
some extent, can be decided by the number of places which can occur chemical re-action in gas diffusion electrode.

3.2. The phenomenon of electrolyte fingering as observed from topological simulations

3.2.1. Fingering

The initial conditions of the simulation were set according to the actual experimental conditions. There is no liquid in the lattices inside gas diffusion electrode. The lattices in the horizontal axis stood for the lower surface of the electrode, that is the liquid boundary condition. There was liquid in every node on the horizontal axis. The top is gas boundary condition, free end. The direction of the vertical axis is electrode’s thickness direction, the area of the picture is 145 μm, accounting for about 1/7 of the total thickness of the actual electrode.

Fig. 6 shows the simulated results of our model. It is liquid distribution when immersion process continues to a particular stage. The red pipelines represent the regions with no liquid, while the blue pipelines are those that are immersed by liquid.

3.2.2. Simulation result analysis

Fig. 6a represents the initial stage of the immersion charges on a gas diffusion electrode. The liquid stayed on the surface of the electrode, only a little liquid is immersed in gas diffusion electrode, the interface of electrolyte inside the porous gas diffusion electrode is distributed like a flat. The gas, liquid and solid phase boundaries just existed on the surfaces of the reaction layer. It has not reached its limit, so discharge performances have not yet reached its optimum.

In Fig. 6b and c the liquid in the porous electrode show signs of “fingering” — a phenomena in which the liquid rises along the inter-connected hydrophilic pipelines within the gas porous electrode. The number of nodes of gas-liquid dividing line in lattice continuously increase with time indicating that the gas, liquid, solid, three phase boundaries are expanding. At this stage the liquid with horizontal infiltration had not yet connected to form a whole. There were enough aisles in the air to support the occurrence of chemical reaction on three-phase boundary, so when the liquid interface progressed from the status in Fig. 6b and c, discharge performances promoted than that at the beginning.

Due to the uneven distribution of hydrophobic material in the PTFE emulsion solution, some hydrophobic pipelines are better distributed at the center in the micro level. The liquid interface now assumes the form as that shown in Fig. 6d. In the electrode, there are several died gas zones caused by the liquid infiltration in the horizontal direction. These areas are labeled ①②③④ in Fig. 6d. These inactive zones
Fig. 6. Gas liquid phase distribution diagram of gas diffusion electrode in immersion process (a–k).
were isolated by the progressing liquid. After O\textsubscript{2} in the inactive gas zones were consumed ultimately, the resulting chemical reactions stop as well. By this time, the chemical reaction took up the regions where the electrolyte had initially occupied, obstructing the mass transfer process and further hindering the discharge process.

As the immersion process progressed, the liquid went quickly along the hydrophilic pipelines, which caused part of the liquid break through electrode. As a result, small droplets merge on the surface of the gas diffusion electrode, which covered the effective micro-pore nearby the broken micro-pore. The three-phase boundary in part of the capillary disappeared. The length of three phase boundary shortened gradually. On the other hand, the number of inactive gas zone gradually increased. Places where chemical reactions can occur inside gas diffusion electrode became lesser and lesser. As the immersion process proceeds, the interface of electrolyte separated from the liquid boundary and the mass transfer distance got longer. Although there were no more inactive gas zones, mass transfer was a laborious process, which negatively affected the discharge rate.

### 3.2.3. Topology simulation and verification of peak power of electrode discharge

According to the Eq. (13), the precise values of every contact angle—\(\theta\) in every tiny pipeline was necessary in order to determine the specific time of the immersion process as shown in Fig. 6. However, these results were hard to measure in actual experiments. In addition, immersion time is sensitive to the specific value of \(\theta\), which is why estimating from figures can cause several errors. However, we also found the immersion volume was not influenced by the uncertainty \(\theta\). We defined the interface points referred to the lattice points connecting to the gas boundary contained by a gas-liquid boundary, micro-pore immersed referred to the crude blue gridlines from liquid boundary developing upwards in the picture. After that, we summarized the correspondence between the interface points and pores immersed from Fig. 6. Fig. 7 shows the relationship between three phase boundary length in actual electrode and the immersion volume.

Comparing Fig. 7 with Fig. 5, the interface nodes and peak power curve followed the same change law in this case. The first 2 points in Fig. 7 exhibited some serious deviation primarily due to the fact that at the beginning the immersion speed was quick. When we measured the first point, the immersion process inside electrode had already rapidly developed too far away. This however deviation did not cause severe impacts to results. According to Fig. 8, the rationality of this simulation has been proved.
3.2.4. Summary of the regularity of the length of three phase boundaries

Here we showed that the discharge performances in gas diffusion electrodes have a direct relationship with three phase boundary length. As immersion process goes on, the length initially lengthens and gradually shortens, conforming to peak-power change law.

![Graph showing the relationship between interfacial nodes and immersion time.](image1)

**Fig. 7.** The relationship between the number of interfacial nodes and the amount of immersion at the infusion time shown in Fig. 6.

![Graph comparing interfacial nodes with experimental peak power.](image2)

**Fig. 8.** The comparison of the relationship between the number of interface nodes and the experimental peak power with the amount of immersion.
4. Conclusion

The network topology model has been simplified and approximated comparing to complex pore structure inside actual porous gas diffusion electrode.

I. In the actual porous electrode, there are lots of narrow slits and irregularly shaped micro-pores. In actual liquid immersion process the pores do not have a circular cross-section as assumed in this article.

II. The actual porous electrode has a 3D stereoscopic structure, the regulation in 2-dimensional lattices vary from actual 3D stereoscopic in some details.

III. The distribution of micro-pore, angle, connectivity and other physical parameters is random, which is different from the uniform lattices in this assumption.

IV. Pores inside actual porous electrode have a different aperture. We only simplify it to three kinds of pores, so there are some differences between assumption and actual situation.

Adding up all these four points, liquid interface inside actual gas diffusion electrode advancing process may vary from the assumptions made in this article. Adding the above improvements to the lattice model, the three-phase boundary mutative trends do not change dramatically. The three phase boundary inside the porous media lengthens gradually, after partial liquid breaking through porous media, partial three phase boundary starts to disappear and the lengths of three phase boundary starts to decline.

Declarations

Author contribution statement

Mei Zhu: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Haosen Ge: Conceived and designed the experiments; Performed the experiments; Wrote the paper.

Xianzhi Xu: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data.

Qian Wang: Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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