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Study on the Dynamic Start - up Ability of Proton Exchange Membrane Fuel Cell with Different Stoichiometric Ratios

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Due to the complexities and changes in operating conditions, the impact of dynamic load on the vehicle fuel cell engine has attracted much attention. Dynamic response of fuel cell affects the performance and life of the battery on a certain extent. And it is one of the obstacles to commercialization. This paper aims to study the dynamic response characteristics of proton exchange membrane fuel cell in dynamic load change. In this paper, the dynamic response characteristics of proton exchange membrane fuel cell were studied by means of transient test method and theoretical analysis. The internal response of the proton exchange membrane fuel cell was analyzed by theoretical analysis combined with air oxygen comparison test and dynamic response characteristics under different oxygen concentration Elaborated. The main research contents were as follows. When the air or oxygen was tested in low gas stoichiometric ratio 1.2 at the same time, the air high current density area obviously occurred transient gas shortage, and the negative of lowest voltage value also occurred. The undershoot of oxygen almost did no increase with the increases of current density step, and maintained at 0.03V. And the response time increased between 0.02s-0.3s. However, in the air test, the undershoot and response time showed a significant increase in linear with the increase of current step, and the value of undershoot was in 0.03v-0.45v, and the response time was in 0.1s-20s. When the air and oxygen flow rate was same, then the undershoot value of oxygen still maintained in 0.03v. But excessive oxygen damaged the battery water balance, resulting in a significant increase in response time. With the increase of oxygen concentration, the dynamic response was low and the response time decreased linearly. So that the dynamic response was mainly caused by mass transfer.

1. Introduction

As a clean energy with high energy conversion efficiency, environment-friendly and low noise, fuel cell is considered the century preferred cleaning and efficient power generation technology (Pandiyan et al., 2013).
Fuel cell is a power generation device that converts chemical energy stored in fuel and oxidant directly into electrical energy without combustion (Flick, et al., 2014). The work process is actually the reverse process of electrolytic water. The basic principle was proposed by William Robert Grove who was lawyer and physicist the British, he is the first to achieve the reverse reaction of electrolysis and generate current scientists in the world. People have researched fuel cell about one hundred year, but it has not been widely used, and it is only used in special fields such as aerospace (Wang, et al., 2016). Only in the past 10 years, with the enhancement of the awareness about the environmental protection, energy conservation and the protection of limited natural resources, the fuel cell began to get attention and development (Jourdan, et al., 2014). When the battery works, it is necessary to deliver the fuel and oxidants into the battery, and to discharge reaction products, while discharging a certain amount of waste heat. It does not go through the heat engine process, so it is not limited by the Carnot cycle.
There are many types about fuel cell, it can be divided into several types according to the type of electrolyte, including alkaline fuel cell, phosphoric acid fuel cell, molten carbonate fuel cell, solid oxide fuel cell and fuel cell (Li et al., 2015). The fuel cell has the characteristics of high energy conversion efficiency, no pollution, rapidly start in low temperature, long life and high power density (Pei et al., 2014). It has become a hot topic in

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the world. This paper focused on the dynamic response of the fuel cell itself to explore the study, and to find a dynamic response to low-voltage overshoot voltage changes in the law.
Basics of PEMFC, the basic voltammetric curves are divided into three polarized regions, activated overpotential regions, resistive overpotential regions, and concentration overpotential regions (Bvumbe, et al., 2016). In this area, the reduce of the voltage due to the influence of the mass transfer limit. In this case, since the mass flow rate limits the rate at which the chemical reaction takes place, the potential reduces. The output voltage of the fuel cell can be expressed as a reversible battery voltage minus the activation loss, the concentration overdischarge and the difference between the ohmic impedance of the electrode and the catalyst layer and the proton film. As shown in the following equation.

$$V = E - \eta_{conc} - \eta_{ohmic} - \eta_{act} \tag{1}$$

The catalyst layer is the core of the fuel cell. The electrochemical reaction takes place here, that is, the reactants are chemically changed. The reaction rate at which the reactants change is associated with the current density of the catalyst surface. In the catalyst layer for the electrochemical reaction, a mathematical model of current density is established by an equation.

$$i_{anode} = i_{O.anode}\left(\frac{C_{\cdot H_2}}{C_{\cdot O.H_2}}\right)^{r_{anode}} \cdot \left(\exp\left(\frac{\alpha_a F \eta_a}{RT}\right) - \exp\left(\frac{-\alpha_c F \eta_a}{RT}\right)\right)$$

$$i_{cathode} = i_{O.cathode}\left(\frac{C_{\cdot O_2}}{C_{\cdot O.O_2}}\right)^{r_{cathode}} \cdot \left(\exp\left(\frac{\alpha_a F \eta_C}{RT}\right) - \exp\left(\frac{-\alpha_c F \eta_C}{RT}\right)\right) \tag{2}$$

2. Experiment and methods

2.1 Test the single cell

MEA was provided by Wuhan Institute of New Energy, and the self-made gas diffusion layer was used. The single cell was standard single cell of USFCC in test, and the active area of the battery was 50cm2. The built-in heating rod was used to heat, and external heating zone was put to keep coherence of the anode and cathode gas pipeline temperature and experimental set gas temperature.

2.2 Test equipment

The equipment of experimental test used the 850C fuel cell test system, which produced by the US company of scribner associates@ company, and the digital oscilloscope of wave runner L T344 was used which produced by the company of LeCroy to conduct accurate voltage measurement of the voltage waveform to correct the test system error.

2.3 Measure the current setting

The battery test system was used to pre-set the current density setting and to change the test conditions to test PEMFC (Horde et al., 2012). Each time the battery was activated to detect the most suitable working conditions for battery operation. And then used a constant current mode to control the load load, to change the current step size ΔI, to explore the changes of undershoot of ΔV and the response time of ΔT in fuel cell. To take ΔI, respectively, 200ma/cm2, 400mA/cm2, ran at each current density, while repeatability verification. Predecessors had three main mechanisms, hysteresis effect and mass transfer diffusion limit. The ohmic impedance transient change was occurred, because the double layer discharge rate was not enough and the water transient changed. For the previous study of the mechanism, the contrast experiment was carried out in the same step current density, the same humidification as well as the battery temperature, the same air pressure, the same stoichiometric ratio of the cathode air and oxygen, the transient change of the internal resistance was analyzed by the usage of HFR.

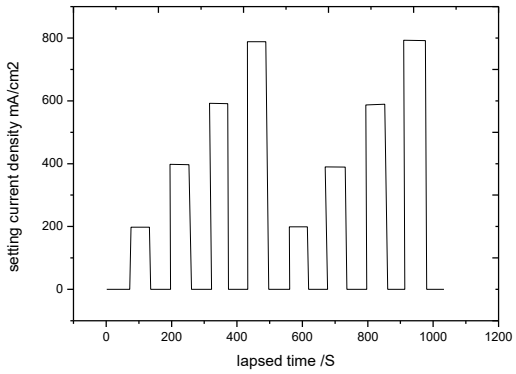

Figure 1: Current density setting

3. Results and analysis

3.1 Dynamic performance comparison of oxygen or air

Anode gas temperature was 50 °C, cathode gas temperature was 45 °C, and the battery temperature was 50 °C. Anode gas and cathode gas excess ratio were all 1.2. It was clear that the air in the high current density area and the big step had been a serious lack of gas, whether the undershoot voltage value, performance voltage or response time value was very bad. As indicated by the arrows in Figure 2, the dynamic response of air PEMFC was extremely poor, while oxygen showed excellent undershoot response performance. From the previous theoretical analysis, low current density area due to empty one-time low-voltage current adjustment was small, so the sudden change in oxygen concentration was not obvious. When the step current was greater than 200mA/cm^2, the air's dynamic response performance was greatly degraded. While the undershoot of oxygen was not affected by the step current, but it required more response time to achieve the required oxygen concentration. The air needed to reach the desired current density for the required oxygen concentration and more time was required. As it was shown in figure 2, when the air or oxygen was tested in low gas stoichiometric ratio 1.2 at the same time, the air high current density area obviously occurred transient gas shortage, and the negative of lowest voltage value also occurred. The undershoot of oxygen almost did no increase with the increases of current density step, and maintained at 0.03V. And the response time increased between 0.02s-0.3s. However, in the air test, the undershoot and response time showed a significant increase in linear with the increase of current step, and the value of undershoot was in 0.03v-0.45v, and the response time was in 0.1s-20s.

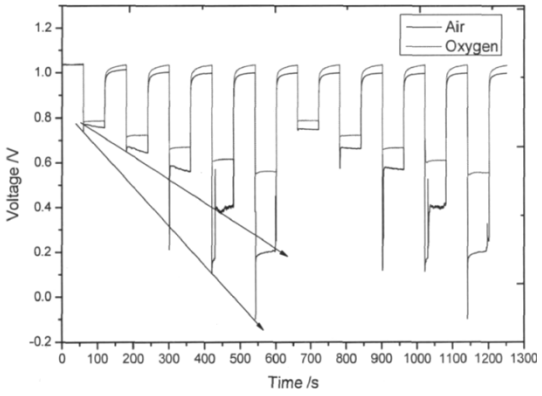

Figure 2: Cathode air/oxygen under same operation condition

The same air-oxygen test conditions, but its undershoot performance was very different, indicating that the gas concentration on the dynamic response of the battery had a great impact. When the gas stoichiometric ratio was set, the internal resistance caused by the electric drag was completely determined by the same current density step, consistent with the previous analysis, but the dynamic response performance was low

and the required Time was far apart, and oxygen concentration was the only explanation. But still the other two "loopholes". First, in this time, the gas flow was not enough, when the step current will be more negative, so the dynamic response performance may be affected by the battery performance. Second, the same stoichiometric ratio, air and oxygen of the gas flow rate was not the same. From the previous theoretical analysis, when the gas flow rate was different, it may cause the difference between the thickness of the diffusion layer and affect mass transfer. The same gas flow rate and sufficient air oxygen as the cathode reaction gas for experimental verification were used in finger 3.

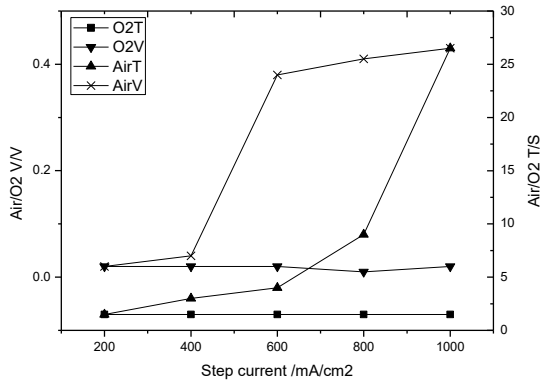

Figure 3: Step current vs air/oxygen undershoot/response time

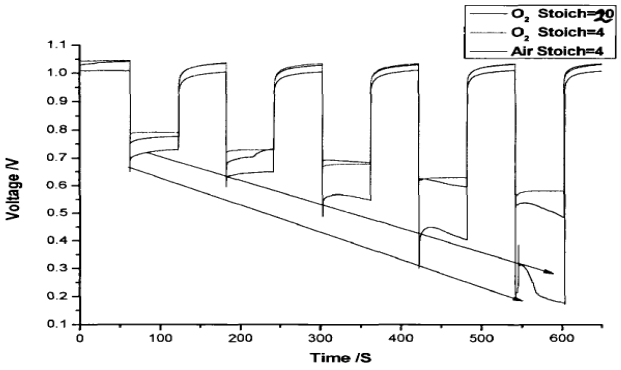

Figure 4: PEMFC dynamic performance under different oxygen stoich

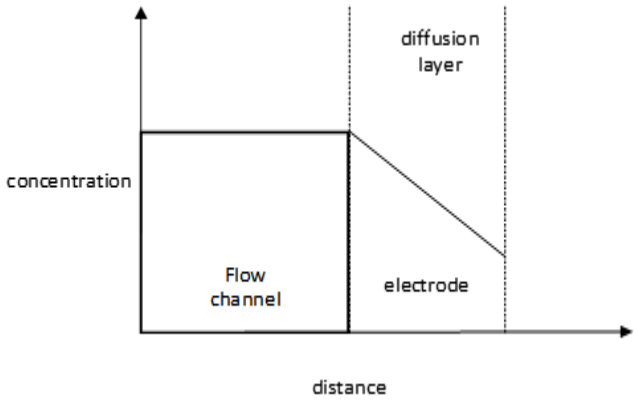

Figure 5: Gas diffusion layer forming when fuel cell works

When the oxygen stoichiometric ratio was 4 and 20, the stoichiometric ratio of air was 4, and the oxygen and air flow rates were the same, the low change of oxygen was very small, but the time that was required for stabilization was greatly increased. It indicated that the relatively fast flow rate damaged the temperature of the gas inside the battery. At this moment, the humidification temperature and the battery temperature of the battery were as the following. The temperature of the battery was 60°C, the temperature of the anode was 50°C, the temperature of the cathode was 60°C, the undershoot value of the air PEMFC and the response time were increased by liner. When the stoichiometric ratio was 1.2, the trend of rapid improvement was different.

Figure 5 showed the "dividing line" of convection-based flow and diffusion-dominated flow, or where the boundary often occurred at the point where the fuel cell gas flow channel and the porous electrode were in contact. The convection within the flow channel caused the air stream to mix well, so there was no concentration gradient. But because of the friction, the movement of the air approached the zero at the electrode-runner boundary. And due to the lack of convective mixing, the concentration of the gas in the gas in the electrode can form a concentration gradient, which we call the gas diffusion layer or the condensed region. Because the boundary between the end of the convective transmission and the diffusion transmission was blurred, and the precise thickness of the diffusion layer was difficult to define. Moreover, the boundary also changed vary with the flow conditions, the geometry and size of the flow channel, and the structure of the electrode. For example, where the gas flow rate was very low, the diffusion layer extended into the middle of the flow channel. Conversely, at very high gas flow rates, convective mixing will penetrate into the electrode, resulting in thinning of the diffusion layer.

3.2 Dynamic performance at different oxygen concentrations

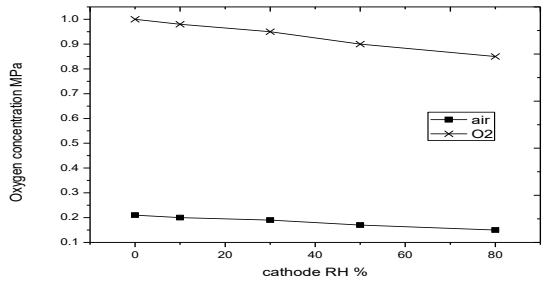

Figure 6: Oxygen concentration of cathode under different humidifier RH

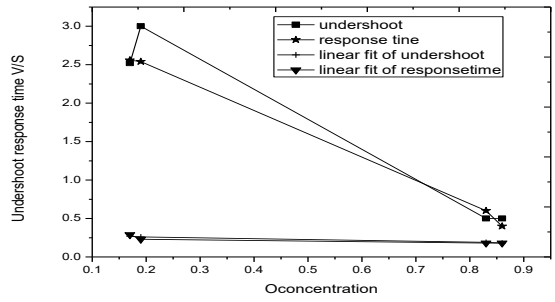

Figure 7: Relationship between oxygen concentration and undershoot, response time

Different humidification humidity of the cathode will bring about changes in the gas concentration inside the cathode runner. Figure 6 was a simple calculation. Basically, the oxygen concentration was linearly related to humidity. Combining the humidification and stoichiometric ratios of air and oxygen in figure 6 and figure 7, different oxygen concentrations can be calculated. At the same time the corresponding dynamic ring should be performanted. Taking the step current density as an example, the influence of stoichiometric ratio on the concentration and the influence of the difference of inlet and outlet density were neglected. With the increase of oxygen concentration, the undershoot and the time that was required decreased linearly. But the above

mentioned, the response time also needed to consider the impact of flow. When the concentration did not change, the flow rate was too large, causing the internal dry, and the response time also increased later.

4. Conclusion

First, when the air or oxygen is tested in low gas stoichiometric ratio 1.2 at the same time, the air high current density area obviously occurs transient gas shortage, and the negative of lowest voltage value also occurs. The undershoot of oxygen almost does no increase with the increases of current density step, and maintaining at 0.03V. And the response time increases between 0.02s-0.3s. However, in the air test, the undershoot and response time shows a significant increase in linear with the increase of current step, and the value of undershoot is in 0.03v-0.45v, and the response time is in 0.2s-20s. Second, When the air and oxygen flow rate is the same, then the undershoot value of oxygen still maintains in 0.3v, but excessive oxygen damages to the battery water balance, resulting in a significant increase in response time. Last, with the increase of oxygen concentration, the dynamic response is low and the response time decreases linearly.

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