

Output Performance of PEMWE under Fluctuating Working Conditions

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Abstract. The fluctuation current introduced by renewable power sources often fluctuates in a wide power range due to their own fluctuation, greatly affecting the performance and safety of the electrolysis cell. Therefore, the input power of PEM water electrolysis process is variable, and it needs to be adjusted in combination with its dynamic characteristics during operation to ensure its performance and safety. In the transient model, research has found that under the condition of step voltage, the current density rapidly decreases, then rapidly increases, rises to the highest point, and slowly decreases before finally stabilizing. On the contrary, under the condition of step flow rate, the current density response is slow and takes about 8 seconds to stabilize.

Keywords: PEMWE, Electrolytic cell performance, Voltage step, Transient model, flow rate step.

1. Introduction

In response to the increasing energy security and climate issues, as well as new challenges to ecological environment protection, actively developing clean energy has become a broad consensus and concerted action among countries around the world to promote energy revolution [1], promote energy structure transformation, and achieve green development.

The proton exchange membrane electrolysis hydrogen production technology has the advantages of simple structure, environmental friendliness, high working current density, good hydrogen precipitation purity, fast start-up speed of the electrolysis cell, and high compatibility with renewable power sources [2]. It is considered the most promising green water hydrogen production technology in the future.

The internal material transfer of proton exchange membrane electrolysis cell mainly includes the transfer of water inside the electrolysis cell, as well as the cross transfer of various internal gases [3]. From this, single-phase models and gas-liquid two-phase models can be established, but there is relatively little research in this area.

The combination of renewable energy sources such as wind and solar energy with PEM electrolysis of water to produce green hydrogen has a very broad prospect. However, the inherent volatility of wind and solar energy often leads to fluctuations in a wide power range [4]. Therefore, the input power of PEM water electrolysis is variable, and it is necessary to adjust its dynamic characteristics during operation to ensure its performance and safety [5].

The fluctuation current introduced by renewable power sources (solar and wind) often fluctuates in a wide power range due to their own fluctuation, greatly affecting the performance and safety of the electrolytic cell. However, there is currently a lack of research on heat and mass transfer inside the electrolytic cell under fluctuating conditions [6].

2. Model description

This article is based on COMSOL software to establish three-dimensional, single-phase, non-isothermal, and transient models. By analyzing the polarization curve and membrane temperature

distribution during the step process, the influence of voltage step on the output performance of the electrolytic cell is explored.

The potential corresponding to the start of the electrolysis reaction of water is the open circuit voltage (E_{ocv}). In the actual working process of the electrolysis cell, there are usually three types of polarization: electrochemical polarization, concentration polarization, and Ohmic polarization. The corresponding overpotential is called electrochemical overpotential (or activation overpotential), concentration overpotential, and Ohmic overpotential.

The voltage of the electrolytic cell is the sum of the open circuit voltage and various overpotentials:

$$V_{cell} = E_{ocv} + \eta_{act} + \eta_{ohm} + \eta_{diff} \quad (1)$$

In the formula: η_{act} is the activation overpotential;

η_{ohm} is the overpotential in ohms;

η_{diff} is the diffusion overpotential.

The magnitude of electrode potential depends not only on the type of electrochemical reaction itself, but also on reaction temperature, concentration of relevant substances, pressure, etc. Nernst theoretically derives the relationship between electrode potential and concentration (or partial pressure), temperature [21], and the open circuit voltage E_{ocv} is obtained from Nernst's equation:

$$E_{ocv} = E_{eq} + \frac{RT}{zF} \ln\left(\frac{\alpha_{H_2} \alpha_{O_2}^{0.5}}{\alpha_{H_2O}}\right) \quad (2)$$

Among them, R - universal gas constant, J/ (mol. K);

F - Faraday constant;

T - working temperature, K;

α_k - activity of various substances;

E_{eq} - Balanced voltage.

The relationship between electrode surface potential and current in electrochemical reactions in proton exchange membrane electrolysis cells can be described using the Butler Volmer equation

$$i_v = \alpha_v i_0 \left[\exp\left(\frac{\alpha_a F}{RT} \eta_{act}\right) - \exp\left(\frac{\alpha_c F}{RT} \eta_{act}\right) \right] \quad (3)$$

$$i_0 = i_{0,ref} \prod_i \left(\frac{C_i}{C_{i,ref}}\right)^{\frac{\alpha_a \nu_i}{n}} \prod_i \left(\frac{C_i}{C_{i,ref}}\right)^{-\frac{\alpha_c \nu_i}{n}} \quad (4)$$

In the formula, α_v - active specific surface area, 1/m

α_a - The charge transfer coefficient of the anode;

α_c - The charge transfer coefficient of the cathode;

i_0 - Exchange current density, A/cm²;

C_i - the concentration of the substance;

ν_i - the stoichiometric coefficient;

i_{ref} -the reference exchange current density.

3. The influence of voltage step on the output performance of PEMWE

Before 0.2 seconds, the voltage of the electrolytic cell is set to 2V, and the electrolytic cell runs stably. Starting from 0.2s, the voltage drops from 2V to 1.5V, and the polarization curve and membrane temperature distribution begin to change rapidly.

3.1. Electrolytic cell output performance

Before $t=0.2s$, the electrolytic cell runs stably, and the current density is 1.5243 A/cm². At $t=0.2s$, the voltage drops from 2V to 1.5V, and the current density responds instantaneously, dropping from 1.5243 A/cm² to 0.0676 A/cm², then rapidly increasing, reaching the highest point and slowly decreasing before finally stabilizing. Figure 1 shows the variation of current density over time when

the voltage of the electrolytic cell steps from 2V to 1.5V. Therefore, the change process of current density mainly consists of three stages: (1) the instantaneous decrease of current density; (2) The current density rapidly increases; (3) The current density slowly decreases. Firstly, the transmission speed of electricity is faster than the transmission process of components, and the response speed is faster. Therefore, when the voltage decreases, the current density also instantly decreases. Secondly, the decrease in voltage and current density means a decrease in electrolytic performance, resulting in a decrease in oxygen produced by the catalytic layer. As the original gas in the flow channel is carried out of the electrolytic cell by liquid water, oxygen in the catalytic layer is more easily transported from the diffusion layer to the flow channel. The proportion of water in the catalytic layer increases, and the concentration of reactants increases, promoting the progress of electrochemical reactions. Therefore, the electrolytic performance improves, and the current density rapidly increases.

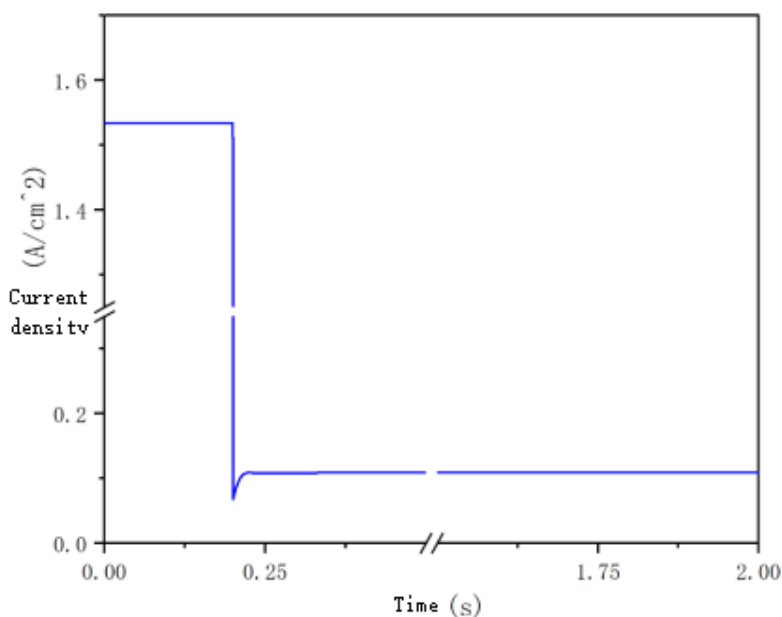


Figure 1. Curve of current density over time

3.2. Membrane temperature distribution

When $t=0.2s$, the voltage steps from 2V to 1.5V, but the membrane temperature remains almost unchanged. This is because the current mutation caused by the voltage step is too rapid and the holding time is very short, resulting in very little Ohmic heat generated. When $t=0.4s$, the current density has basically stabilized. At this time, due to the short time, the average film temperature only slightly decreases. When $t=2s$, heat transfer is in a steady-state process, and the film temperature distribution at this time is the film temperature distribution with a steady-state voltage of 1.5V. Figure 2 shows the variation of proton exchange membrane temperature over time when the voltage of the electrolytic cell steps from 2V to 1.5V.

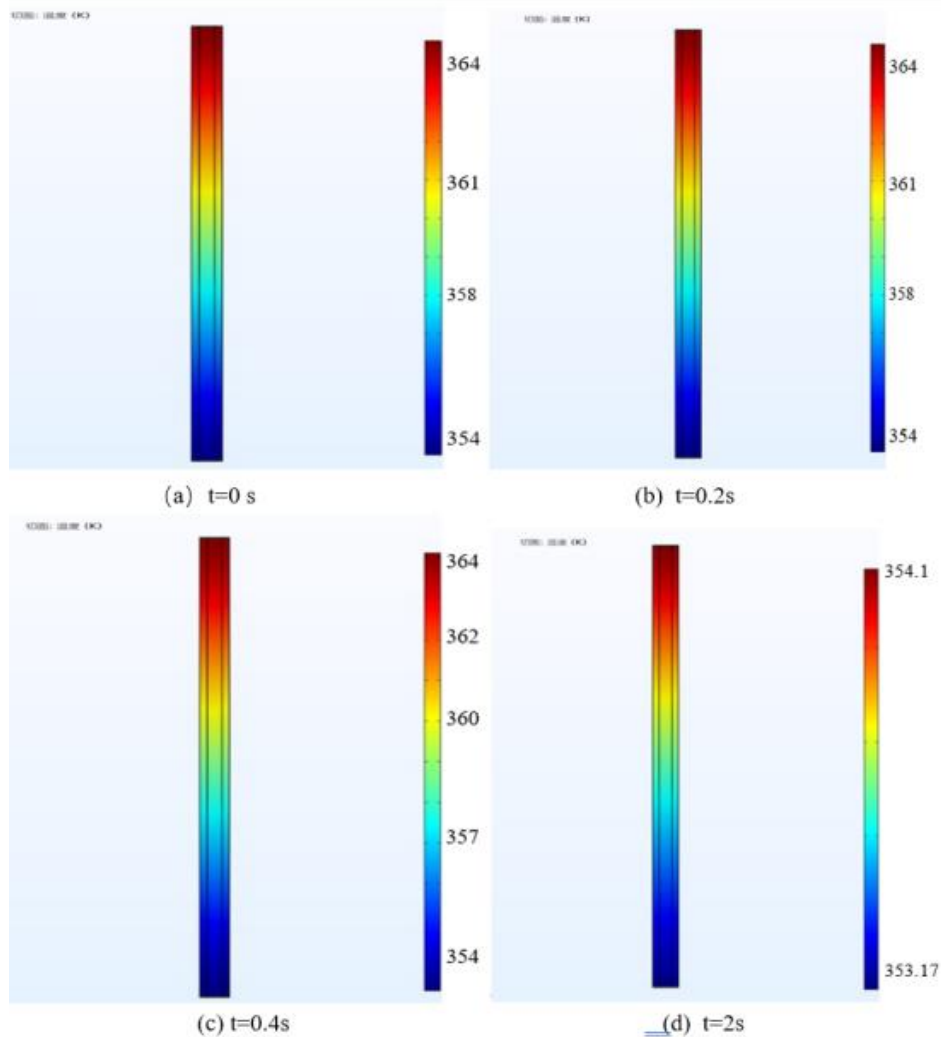


Figure 2. Membrane temperature distribution at different times

3.3. Distribution of current density in catalytic layer

When $t=0.2s$, the voltage steps from 2V to 1.5V, and the current density rapidly decreases. The highest current density drops from $1.61 \times 10^4 A/m$ to $1.23 \times 10^3 A/m$, and then rebounds to $1.36 \times 10^3 A/m$. This is because the transmission speed of electricity is faster than the transmission process of components, and the response speed is faster. Therefore, when the voltage decreases, the current density also instantly decreases. At $t=0.4s$, the current density of the catalytic layer has tended to remain constant, and the rate of change is much faster than that of the membrane temperature. Figure 3 shows the variation of catalytic layer current density over time when the voltage of the electrolytic cell steps from 2V to 1.5V.

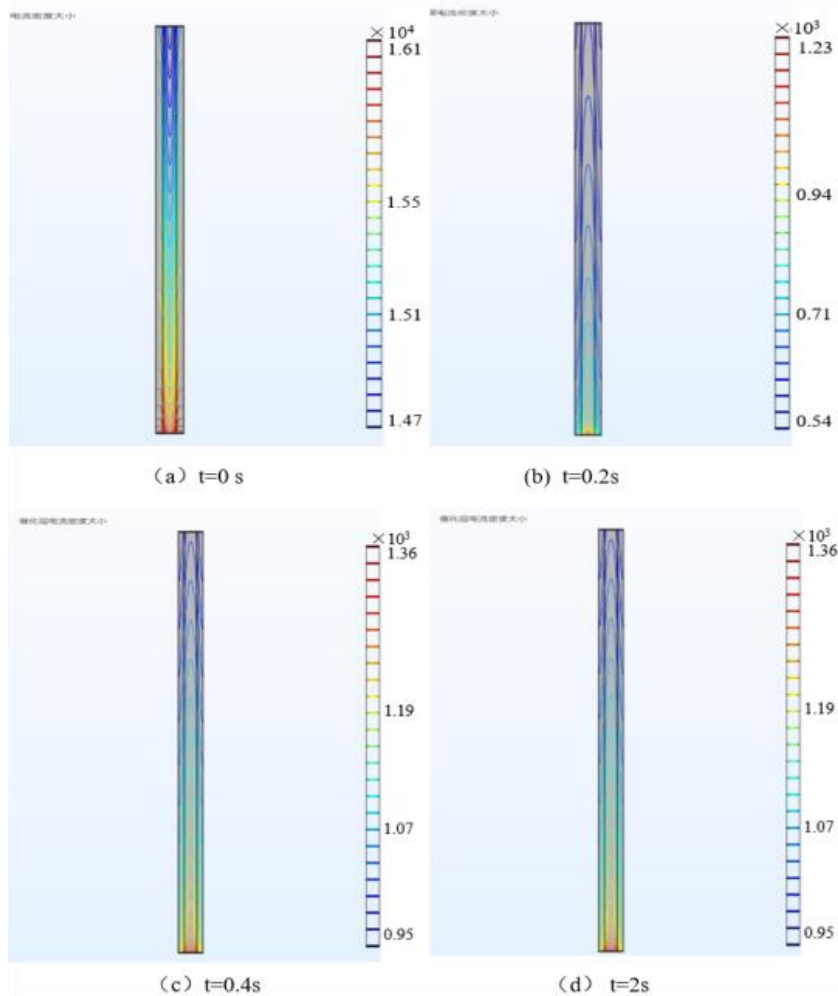


Figure 3. Current density distribution of catalytic layer at different times

4. The influence of inlet flow velocity variation on the output performance of PEMWE

Before $t=0.2s$, the inlet flow rate was $0.25m/s$ and the electrolytic cell operated stably. At $t=0.2s$, the inlet flow velocity steps from $0.25m/s$ to $0.5m/s$. Exploring the influence of flow rate step on the output performance of electrolytic cells by analyzing the polarization curve and membrane temperature distribution during the step process

4.1. Electrolytic cell output performance

Before $t=0.2s$, the electrolytic cell runs stably, and the current density is $1.147A/cm^2$. At $t=0.2s$, the inlet flow rate steps from $0.25m/s$ to $0.5m/s$, and the current density slowly increases to $1.162A/cm^2$. It can be seen that compared to the voltage step, its response speed is extremely slow, and it took nearly 8 seconds for the current density to stabilize. This is because the transmission speed of electricity is faster than the transmission process of components, and the response speed is faster. Therefore, when the voltage decreases, the current density also instantly decreases; The change in flow rate is mainly the result of the comprehensive impact on the output performance of the electrolytic cell by affecting the water content of the catalytic layer and the temperature of the electrolytic cell. Figure 4 shows the variation of current density over time when the inlet flow velocity steps from $0.25m/s$ to $0.5m/s$. From the previous analysis, it can be seen that temperature changes and changes in the moisture content of the catalytic layer are a continuous accumulation process, so the response is relatively slow.

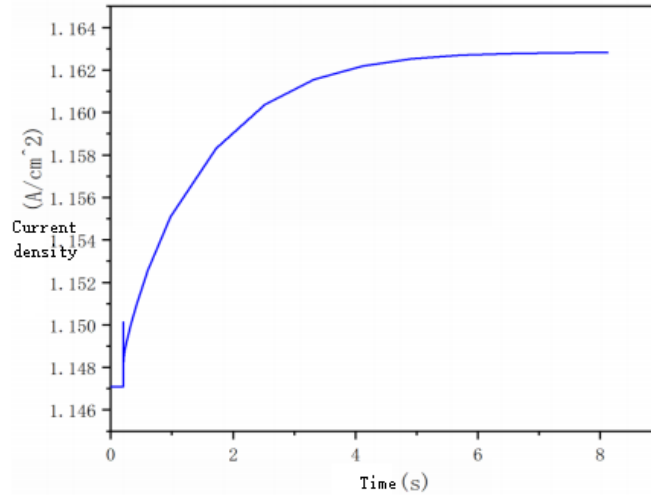


Figure 4. Curve of current density over time

4.2. Membrane temperature distribution

The inlet flow rate steps from 0.25m/s to 0.5m/s, and compared to the change in current density, the change in membrane temperature is a very slow process. It can be seen that with the increase of time, the membrane temperature also decreases continuously. This indicates that the Ohmic heat generated by the increase in current density is less than the heat brought out of the electrolysis cell by the increase in flow rate. Therefore, the membrane temperature continues to decrease. Finally, as the current density stabilizes, the proton exchange membrane temperature also tends to temperature. Figure 5 shows the variation of membrane temperature distribution over time.

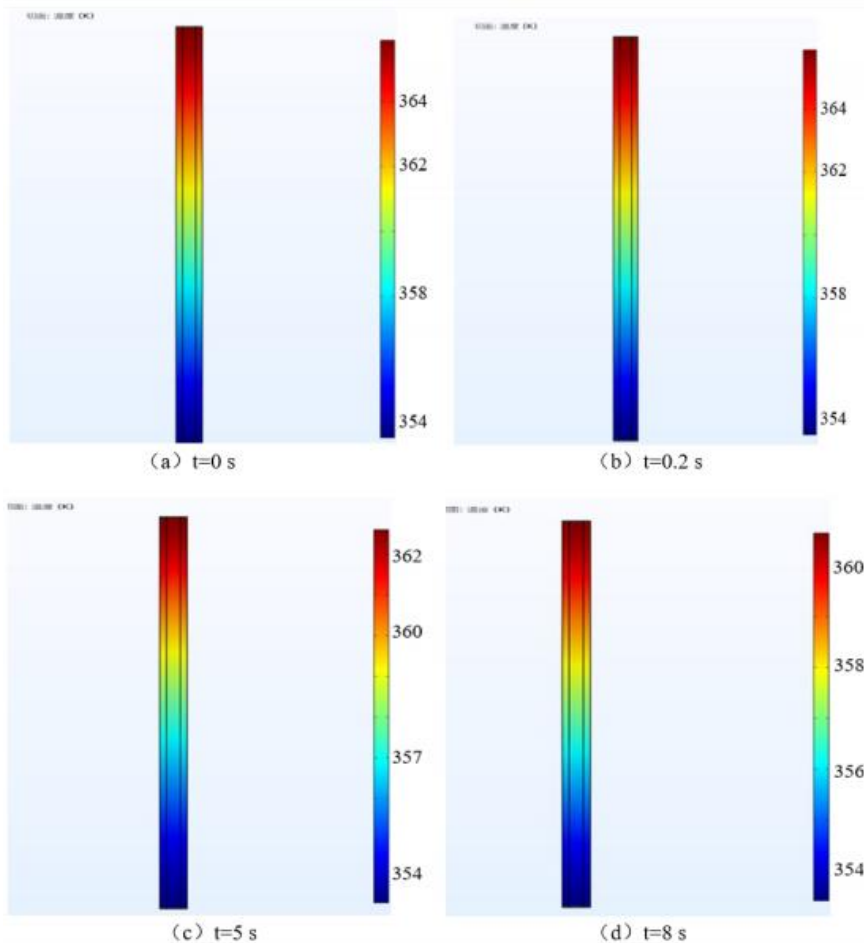


Figure 5. Temperature distribution of membrane at different times

4.3. Distribution of current density in catalytic layer

When $t=0.2s$, the current density slowly increases because the transmission speed of electricity is faster than the component transmission process, and the response speed is faster. Therefore, the current density also instantly decreases when the voltage decreases; The change in flow rate is mainly the result of the comprehensive impact on the output performance of the electrolytic cell by affecting the water content of the catalytic layer and the temperature of the electrolytic cell. From the previous analysis, it can be seen that temperature changes and changes in the moisture content of the catalytic layer are a continuous accumulation process, so the response is relatively slow. Figure 6 shows the variation of catalytic layer current density over time.

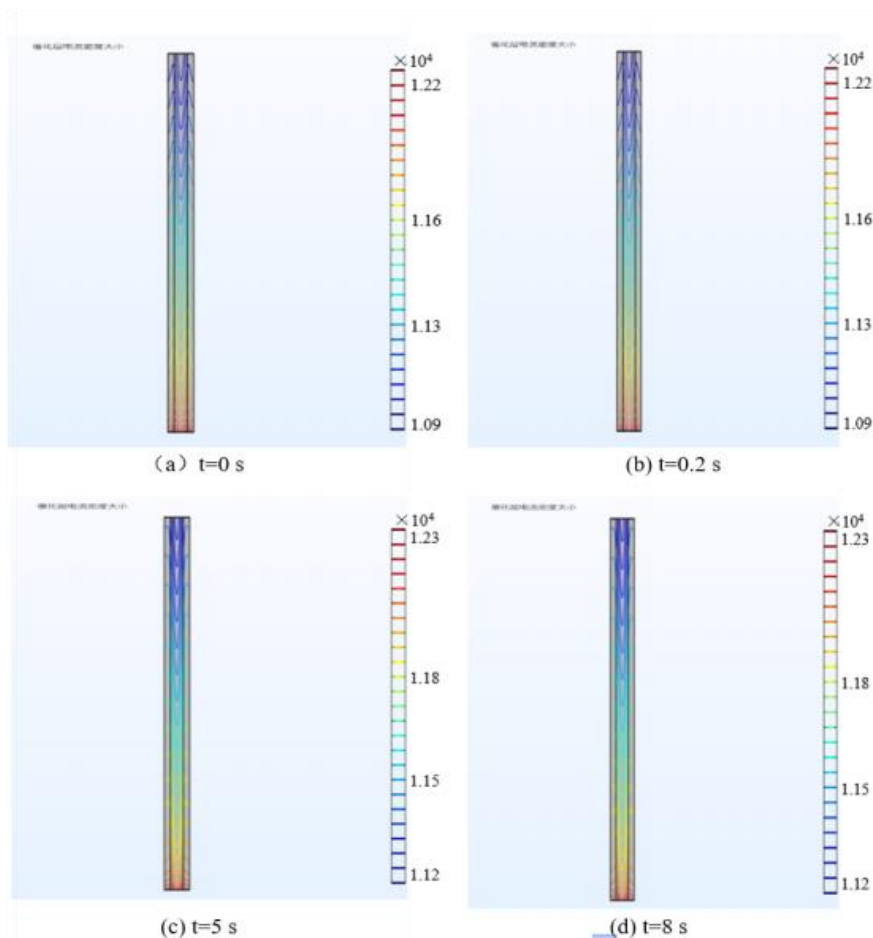


Figure 6. Current density distribution of catalytic layer at different times

5. Conclusion

When the voltage steps, the current density will go through three stages: a rapid decrease, a rapid increase, and then a slow decrease, and a tendency to stabilize. Compared to others, the temperature change of PEM is much slower, and the voltage step has almost no effect on the temperature. This is because the transmission speed of electricity is faster than the transmission process of components, and the response speed is faster. Therefore, when the voltage decreases, the current density also instantly decreases.

When the inlet flow rate steps, it is different from the rapid response of voltage and current density to sudden changes. The current density will experience a slow increase period, lasting for about 8 seconds. The change in flow rate is mainly the result of the comprehensive impact on the output performance of the electrolytic cell by affecting the water content of the catalytic layer and the temperature of the electrolytic cell. Due to the continuous accumulation of temperature changes and changes in the moisture content of the catalytic layer, the response is relatively slow.

Acknowledgments

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