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Analysis of Flow Rate Inducing Voltage Loss in a 100 cm² Class Molten Carbonate Fuel Cell

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ABSTRACT :

This work focuses on the behavior of the overpotential increase due to a utilization rise in a molten carbonate fuel cell. The behavior is generally explained by Nernst loss, which is a kind of voltage loss due to the thermodynamic potential gradients in a polarization state due to the concentration distribution of reactant species through the gas flow direction. The evaluation of Nernst loss is carried out with a traditional experimental method of constant gas utilization (CU). On the other hand, overpotential due to the gas-phase mass-transport resistance at the anode and cathode shows dependence on the utilization, which can be measured using the inert gas step addition (ISA) method. Since the Nernst loss is assumed to be due to the thermodynamic reasons, the voltage loss can be calculated by the Nernst equation, referred to as a simple calculation (SC) in this work. The three values of voltage loss due to CU, ISA, and SC are compared, showing that these values rise with increases in the utilization within acceptable deviations. When we consider that the anode and cathode reactions are significantly affected by the gas-phase mass transfer, the behavior strongly implies that the voltage loss is attributable not to thermodynamic reasons, namely Nernst loss, but to the kinetic reason of mass-transfer resistance in the gas phase.

Keywords: Molten carbonate fuel cell; Nernst loss; Overpotential; Mass transfer; Voltage loss

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1. Introduction

Understanding electrode reactions in a molten carbonate fuel cell (MCFC) is required for its practical development because its performance is determined by the reaction resistance at the electrodes. The resistance is represented in a form of overpotential at the anode and cathode, thus the correct evaluation of overpotential provides clues for the analysis of reaction characteristics. Voltage loss in the MCFC generally comprises ohmic loss (η_{IR}) and reaction overpotentials at the anode (η_{an}) and cathode (η_{ca}); ohmic loss is due to the electrical resistance among the cell components and reaction overpotential is ascribed to the

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resistance in the electrochemical reactions at both electrodes. Thus, output voltage (V) can be expressed as follows:

$$V = E_{OCV} - \eta_{IR} - (\eta_{an} + \eta_{ca}) \tag{1}$$

where, $E_{OCV} = E^o + \dfrac{RT}{2F} ln \left(\dfrac{[H_2]}{[H_2O][CO_2]_{an}} [O_2]^{0.5}[CO_2]_{ca} \right)$

and E^o is the standard potential. Subscripts "an" and "ca" represent the anode and the cathode, respectively. Other symbols have their usual meanings.

The MCFC, which normally runs at around 923 K with carbonate electrolyte, has relatively severe operating conditions: 1) it uses porous electrode with corrosive carbonate electrolytes melting around 773 K; 2) assembly of cell components such as electrodes, electrolyte, and matrices may have standard deviations leading to various performances; 3) the cell is assembled with generally

thin components which do not allow stable installation of the reference electrode in order to analyze overpotential at the electrodes. Complete analysis of the overpotential and reaction kinetics has been obstructed for these reasons.

In previous works, the reaction characteristics of 100 cm^2 class MCFC have been illuminated by several experimental methods: the inert gas step addition (ISA) method,[1] reactant gas addition (RA) method,[2] and water head (WH) measurements.[3] They mostly dealt with gas flow effects on the overpotential, indicating consistently that at the anode a mass-transfer controlling process in the gas phase is principally dominant, whereas at the cathode combined mass-transfer processes in the gas and liquid phases prevail.

As a voltage loss in a MCFC, Nernst loss has been suggested.[4-6] It is based on the assumption that concentration distribution occurs along the gas flow route in a polarization state, and it induces a potential gradient in the cell according to the Nernst equation. Then, the potential difference between the gas inlet and outlet behaves as an overvoltage, which is called Nernst loss. However, the thermodynamic relation of the Nernst equation is assumed to be in the equilibrium state in which the concentrations of reactants are the same everywhere in the cell. It has been reported that MCFC in a polarization state has a vertical concentration distribution from the gas phase to the electrode surface.[1] Thus it is questionable whether the potential calculated from the bulk concentration can represent the electrode potential while the concentration on the electrode surface may have a different value from the bulk due to the concentration gradient in the polarization state.

The dependence of overpotential on the utilization at both electrodes was illuminated by comparing the Nernst loss in the traditional methods with overpotential from another experimental method. As conventional methods, the constant gas utilization (CU) method and simple calculation (SC), which are considered as experimental and theoretical methods of obtaining the Nernst loss, were employed. As another method for the overpotential, inert gas step addition (ISA) method was used. Voltage losses obtained from CU, SC, and ISA were compared for various anode and cathode utilizations.

2. Experimental

The MCFC used in this work had about 100 cm^2 of geometrical surface area of electrode. The anode was a porous thin plate of Ni-Al alloy while the cathode was a

Table 1. Specifications of 100 cm^2 class MCFC components

Components	Specification	
Anode	Material	Ni-Al Alloy
	Pore size	3-4 μm
	Porosity	50-60%
	Thickness	0.77 mm
	Size	100 cm^2
Cathode	Material	NiO (in-situ)
	Pore size	8-10 μm
	Porosity	70-80%
	Thickness	0.72 mm
	Size	121 cm^2
Matrix	Material	LiAlO$_2$
	Pore size	0.3-0.4 μm
	Porosity	55-65%
	Thickness	0.35 mm
Electrolyte	Material	70Li-30 K carbonate
Separator	Material	STS316L

porous thin Ni plate. The matrix was fiber reinforced LiAlO$_2$, and the electrolyte was (70 + 30) mol% (Li+K)$_2$CO$_3$ eutectics. The single cell was operated under an atmospheric condition, and the temperature was kept at 923 K. Table 1 shows detail specifications of cell components. More details of the cell structure and cell operation were described in a previous work.[1]

A mixture of 80 mol% H$_2$ and 20 mol% CO$_2$ was supplied to the anode through the 53°C water bubbler (H$_2$: CO$_2$: H$_2$O = 0.69 : 0.17 : 0.14 atm), while a mixture of 70 mol% air and 30 mol% CO$_2$ was fed to the cathode. Utilization, a ratio of consumed gas amount to feed amount for the anode (u_f) and cathode (u_{ox}) ranged from 0.2 to 0.6 at 15 A. The gas flows were controlled by several MFCs (Mass Flow Controllers).

Steady state polarization has been carried out to obtain the effect of utilization change on the overvoltage. The current was raised from 0 to 15 A with a galvanostat at a fixed reactant flow rate. Then, the total voltage loss could be obtained with respect to the utilization.

As a conventional way to measure Nernst loss, constant gas utilization (CU) has been employed. Fig. 1 shows how to measure the Nernst loss at the anode ($\Delta V_{u,an}$) and cathode ($\Delta V_{u,ca}$) with the CU method. Since the Nernst loss is a function of utilization, a difference between E_{OCV} and an extrapolated voltage to current zero from the current-voltage line of constant utilization is regarded as the Nernst loss at the utilization.

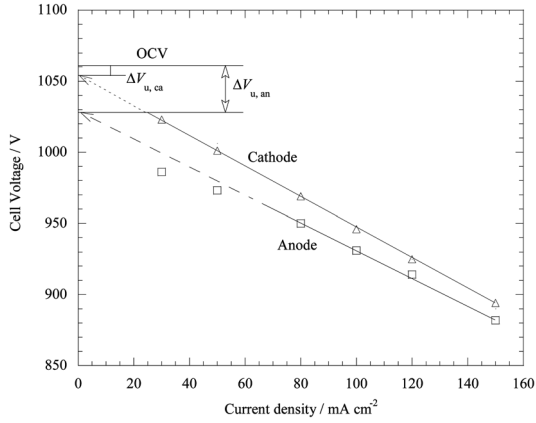$$\Delta V_u = E_{OCV} - V(u, i \to 0) \qquad (2)$$

Fig. 1. Estimation of voltage loss with constant gas utilization (CU) method at the anode ($u_f = 0.2$) and cathode ($u_{ox} = 0.4$), 923 K, 1 atm.

The constant utilization was maintained by controlling the gas flow rate according to the applied currents; thus the gas flow rates were reduced proportionally to the applied currents. The value of $\Delta V_{u,an}$ is much larger than $\Delta V_{u,ca}$ as shown in Fig. 1. Thus it is known that the anode has much larger Nernst loss than the cathode.

As a method for the overpotential measurement, inert gas step addition (ISA) was employed in this work.[1] In the ISA method a certain flow rate of inert gas was added to an electrode where the inlet port for the inert gas was installed about 4 m ahead of anode and about 1.5 m before the cathode separately. Thus there was gas volume between the port and an electrode. The added inert gas drove the reactant gas in the gas volume, which raised flow rate of reactant gas without changing compositions while the inert gas arrived at the cell. Since the flow rate at a fixed current density was corresponding to the utilization which was a ratio between consumed gas amounts to feed amount. Thus the inert gas addition changed utilization of the electrode. Consequently, voltage variation in terms of utilization provided information of overpotential at the electrode. Nitrogen was used as inert gas at the anode and cathode, and its flow rate ranged from 0.1 to 1.0 L min^{-1}. All the gas tubes were stainless steel with outer diameters of 1/4 inches. More detailed characteristics of the ISA method were described in a previous paper.[1]

3. Results and Discussions

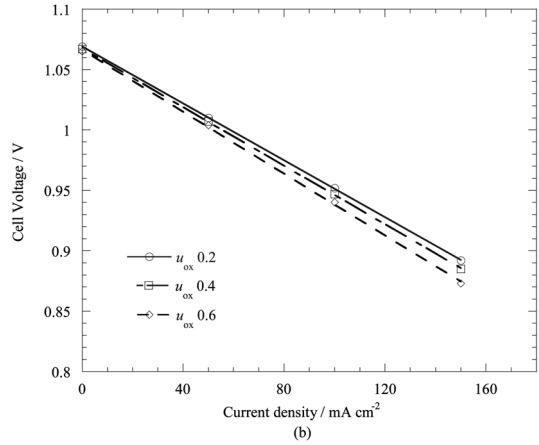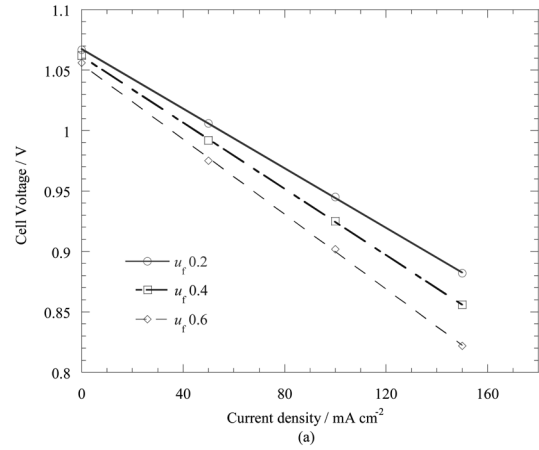Fig. 2 shows the results of steady state polarization (SSP) with respect to the anode (a) and cathode utilizations

Fig. 2. Results of steady state polarization (a) at the anode (cathode flow rate = 0.883 L min^{-1}) (15A), (b) at the cathode (anode flow rate = 0.759 L min^{-1}), 923 K, 1 atm.

(b). Since the utilization is a ratio of consumed reactant amounts to feed amount at a fixed current load, higher utilization means a lower flow rate of reactant gases. The clear dependence of voltage on the utilization and flow rate is observed. The SSP represents total voltage loss due to the difference between output voltage (V) and open circuit voltage (E_{OCV}), and thus it is obvious that a higher utilization has a larger overvoltage. In addition, the distinguishable change in the slope at the anode indicates that the anodic overpotential depends on the flow rate more strongly than the cathodic one does. In general the electric conductivity of the carbonate electrolyte is hardly dependent on the flow rates, and thus the change in flow rate is wholly responsible for the overpotential variation.

In a previous work of Sampath *et al.*,[4] the behavior has been interpreted thermodynamically. Since the cell consumes a certain amount of gas at a fixed current load, a change in flow rate leads to various concentration distributions along the gas flow route. A more severe concentration distribution is expected at a lower flow rate. From a theoretical viewpoint,[7] the potential of a reversible system is determined by the concentration of reactant and product species. Thus the concentration distribution may induce a potential gradient along the gas flow route. A steeper potential gradient occurs at a lower gas flow rate and higher utilization for a fixed current. They suggested that the potential gradient behaves as a voltage loss called Nernst loss. Thus a larger Nernst loss is suggested at a higher utilization and lower flow rate. According to their suggestion, the large voltage loss at a high utilization is due to the significant amount of Nernst loss.

However, Lee *et al.*[1] have suggested that MCFC has a significantly higher reaction rate at the anode and cathode, and thus the reactions at the anode are mass-transfer controlling processes in the gas phase while the cathode reaction is combined mass-transfer limiting processes in the gas and liquid phases from the ISA method. They also reported that the anode overpotential is mostly attributed to the mass-transfer resistance of CO_2 and H_2O under a normal operating condition ($H_2 : CO_2 : H_2O = 0.69 : 0.17 : 0.14$ atm).[2]

Fig. 3 shows the results of ISA measurement with addition of 0.3 L min⁻¹ N_2 at the anode (a) and cathode (b). As reported in a previous work,[1] N_2 addition at the anode immediately raises the voltage because the addition enhances the reactant flow rate without changing the composition. Thus the voltage gain ($\Delta V_{I,an}$) is obtained from the overpotential variation due to the flow rate and utilization change.

Overpotential is generally attributed to the charge-transfer and mass-transfer resistances in the electrode. In the MCFC, the surface of electrodes is covered by thin carbonate electrolyte. Thus, the overpotential reflects series resistance of charge transfer and mass transfers in the liquid and gas phases. Then the following overpotential relation involving the series resistance has been suggested [1].

$$\eta = \frac{iRT}{n^2 F^2 a p_0}\left(\frac{h}{k_0} + \frac{h}{k_L} + \frac{1}{k_G}\right) \tag{3}$$

where, $k_L \cong \dfrac{D_L}{\delta}$ and $k_G \approx 0.664\left(\dfrac{\upsilon_f}{L}\right)^{\frac{1}{2}}$, $(D_G)^{\frac{2}{3}}(v)^{-\frac{1}{6}}(RT)^{-1}$, p_0 is the pressure, h is the Henry's Law constant, a is
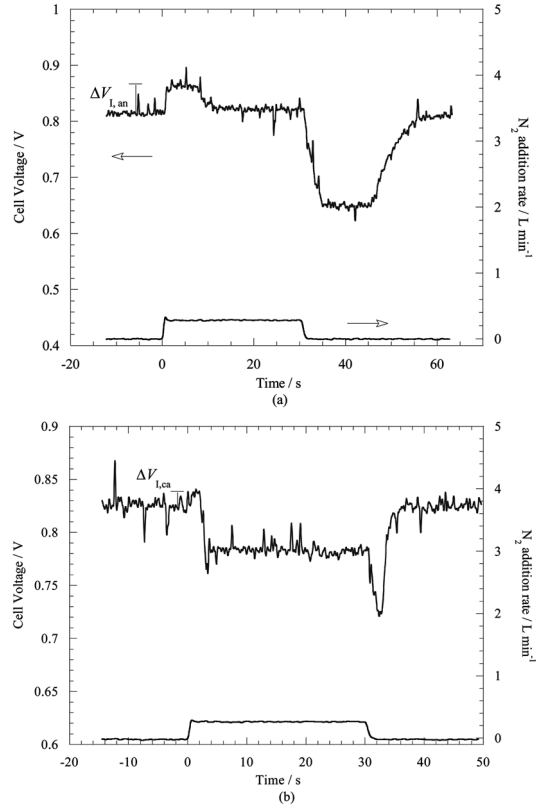

Fig. 3. Voltage patterns by the addition of 0.3 L min⁻¹ N_2 to the anode of total flow rate of 0.253 L min⁻¹ (a) and cathode of total flow rate of 0.883 L min⁻¹ (b) at 923 K, 1 atm.

the geometrical surface area, i is the current, D_L is the diffusivity in the electrolyte, δ is the electrolyte film thickness, υ_f is the average flow velocity in the gas channels, D_G is the diffusivity of gas reactant, L is the electrode length, v is the kinematic viscosity, R is the gas constant. Other symbols have their usual meaning.

Among the resistances only gas-phase mass-transfer coefficient, k_G involves flow rate effect as shown in Eq. (3). A flow rate at a fixed current density can be converted to utilization. Then the overpotential due to the flow rate (h_G) can be expressed by utilization, u.

$$\eta_F \cong \frac{iRT}{n^2 F^2 a p_0}\left(\frac{1}{k_G}\right) = q u^{0.5} \tag{4}$$

where $q = 1.51 \dfrac{R^2 T^2 (iLs)^{1/2} v^{1/6}}{(n^3 F^3 a^2 p_0)^{1/2} D_G^{2/3}}$, $u\left(= \dfrac{\upsilon_C}{\upsilon_F}\right)$ is the anode gas utilization, s is the cross-sectional area of gas channels, υ_C is the amount of gas consumed, υ_F is the

amount of feed gas, L is the electrode length, and other symbols have their usual meanings.

As shown in Eq. (4) overpotential is the function of utilization. The voltage gain, $\Delta V_{\text{I,an}}$, was ascribed only to the flow rate and utilization change.[1] Therefore, the voltage gain can be expressed as follows:

$$\Delta V_{\text{I,an}} \text{ or } \Delta V_{\text{I,ca}} = \eta_{\text{G1}} - \eta_{\text{G2}} = q(u_1^{0.5} - u_2^{0.5}) \qquad (5)$$

where the subscripts 1 and 2 denote before and after N_2 addition, respectively. On the other hand, the voltage gain at the cathode ($\Delta V_{\text{I,ca}}$) is relatively small compared with $\Delta V_{\text{I,an}}$ as shown in Fig. 3(b). It means that the cathode has a smaller mass-transfer resistance in the gas phase than the anode because the cathode has only a deficiency of O_2 species and its slow diffusion process through the liquid electrolyte film prevails.[2]

When we assume that the utilization before the N_2 addition is a constant, then the following equation is available from Eq. (5):

$$\Delta V_{\text{I,an}} \text{ or } \Delta V_{\text{I,ca}} = m - qu_2^{0.5} \qquad (6)$$

Figs. 4(a) and (b) show the relation of Eq. (6) at the anode and cathode, respectively. Since the anode gas flow rate (total 0.253 L min^{-1} at $u_f = 0.6$) is much smaller than that of the cathode (total 0.883 L min^{-1} at $u_{\text{ox}} = 0.4$), the same amount of flow rate increase due to the addition of N_2 (0.1 to 1.0 L min^{-1}) reduces the anode utilization to much a lower value than the cathode utilization. Then we can obtain q values from the slopes: the anodic value of q (q_{an}) is 160.0 mV and the cathodic one (q_{ca}) is 29.5 mV. In addition, we can obtain the
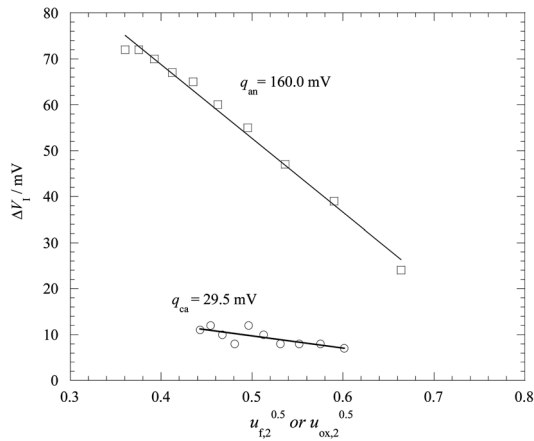
overpotential at various utilizations with Eq. (4).

The overpotential due to the gas-phase transport (η_{G}) was compared with the Nernst loss obtained by the experimental method and calculation. As an experimental method for the Nernst loss, the constant gas utilization (CU) method was employed. An arithmetic mean of potential difference between the gas inlet and outlet (Nst) was also calculated for the Nernst loss as a simple calculation (SC) method. Since the open circuit voltage is a function of temperature and gas compositions (Eq. 1), the different gas compositions at the gas inlet and outlet at a current load give the potential gap of Eq. (7).

$$Nst = (E_{\text{in}} - E_{\text{out}})/2 \qquad (7)$$

Fig. 5 compares the overpotential at the anode ($\eta_{\text{an,G}}$) and the cathode ($\eta_{\text{ca,G}}$) obtained by the ISA
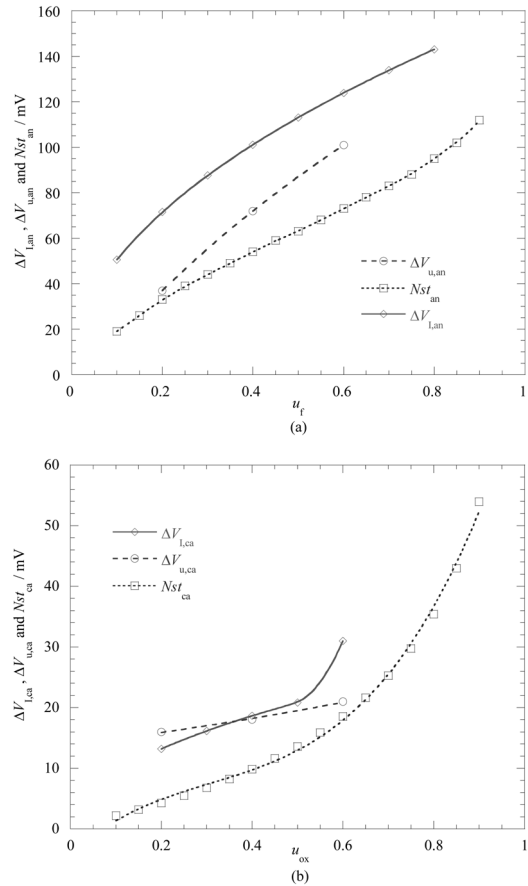

Fig. 4. Relations of Eq. (6) at the anode and cathode with ΔV_{I} obtained from Fig. 3.

Fig. 5. Comparisons of overpotential measured by ISA method (ΔV_{I}) with Nernst loss obtained by CU method (ΔV_{u}) and calculation (Nst) at the anode (a) and cathode (b) at 923 K, 1 atm.

method with the Nernst loss obtained by the CU method ($\Delta V_{u,an}$ at the anode and $\Delta V_{u,ca}$ at the cathode) and SC method (Nst_{an} at the anode and Nst_{ca} at the cathode). Although the values at the anode show some deviation, they have consistency in rising with utilization with a similar slope. Among them, the values are found to be closer to each other at the cathode. As mentioned above, the results of ISA indicate that MCFC has overpotential due to the slow gas-phase mass-transfer process. This implies that the concentration gradient from the gas-phase reactant to the electrode surface exists and the compositions of reactants in the bulk gas are different from those at the electrode surface. However, the Nernst loss was suggested on the assumption of the equality of bulk gas composition with the electrode surface. This is a theoretically unacceptable assumption. Another unreasonable point of Nernst loss is that it cannot reflect electrode conditions such as thickness, pore structure, pore size distribution, and so on. A recent work reported that overpotential due to the gas-phase mass transfer (η_{an}) varies among cells: one cell showed 159 mV of $\eta_{an,G}$ while the other cell showed 189 mV.[8] This indicates that the overpotential depends on the electrode condition. When we consider the similarity between the Nernst loss according to the CU and SC methods and the overpotential found by the ISA method, the voltage loss due to utilization change is ascribed to the kinetic reasons of mass transfer in the gas phase.

4. Conclusion

The voltage loss, which shows larger values at higher utilization, was investigated by comparing the overpotential due to the gas-phase mass-transfer resistance with Nernst loss, a hypothetical voltage loss with thermodynamic backgrounds. The overpotential induced by the gas-phase mass-transfer effect (η_G) was measured using the inert gas step addition (ISA) method, whereas the Nernst loss was obtained by a calculation (simple calculation, SC) method and an experimental method (constant gas utilization method, CU). The measured overpotential with ISA showed a behavior with respect to utilization that was similar to the values of Nernst loss obtained by the SC and CU methods. The Nernst loss, based on the assumption that the cell potential is determined by the bulk gas composition, is a kind of hypothetical value. Considering that a concentration distribution exists through the gas phase over the electrode, the bulk gas composition may be different from that at the electrode surface. Coincidently η_G increases with utilization, allowing η_G to have a similar value to the Nernst loss. When we consider the theoretical vulnerability of the Nernst loss, the voltage loss is ascribed to the kinetic reason of the mass-transfer effect through the gas phase.

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