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Diffusion Phenomena of Silver Ion in Molten Sodium Borate by Chronopotentiometry

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Synopsis

Diffusion phenomena of silver ion in the molten sodium diborate of low silver ion content were investigated at the temperature range from 880°C to 625°C by means of chronopotentiometry.

From the results, it was shown that the silver ion was reduced reversibly to metallic state at the silver electrode used and silver ion was transported only by diffusion in case that transition time in a potential-time relation was within several seconds. Diffusion coefficients measured at various temperatures satisfied Arrhenius equation. The activation energy of diffusion and diffusion coefficient were respectively 32Kcal/mol and 6.5×10^{-7} cm^2/sec at the liquidous temperature. By comparing these values with those obtained in some molten salts, the difference of structure between the molten glass and molten salts was discussed. Moreover, the consideration for the size of borate anion existing in the molten glass was also tried from the viewpoint of rate process and from Stokes-Einstein's equation.

§ 1. Introduction

For a long time, the self diffusion coefficients of main components of glass have been extensively investigated by means of mainly tracer technique in the range from solid state to molten state,$^{1)}$ because the self diffusion is closely related to various properties and processes of glass, that is, viscosity, electrical conduction, strengthening of glass by ion exchange and so on.

On the other hand, the glass containing oxides of transition element shows various interesting properties from the viewpoints of optics, electricity and magnetism. These propetries are considered to be attributed to redox equilibria, diffusion phenomena of metallic ions and behaviors as redox matrix of a base glass. Especially, the diffusion behavior of matallic ions plays an important role on ion exchanging techniques, "chemical toughening" at glass surface and "spectro-float technique" etc..

The authors wish to investigate these redox and diffusion behaviors from electrochemical standpoints. As the first step, we tried to measure the diffusion coefficients of monovalent metallic ion in the molten glass.

There are three methods in the measurement of diffusion coefficient by means of electrochemical technique, that is, polarography, potential sweep method and chronopotentiometry. Polarography, however, is unsuitable, because the comparatively long period of electrolysis causes the composition change of electrolyte and the change of the state of electrode surface. On the other hand, in potential sweep method the accuracy is not satisfactory for irreversible process, because peak current depends on the reversibility of electrode reaction. In chronopotentiometry, it is possible to measure the diffusion coefficient with considerable accuracy, independently on reversibility, in case that experimental conditions are chosen such that linear diffusion is satisfied and convection and condenser current can be ignored. This method has been extensively applied to molten salts having comparatively low meting point since Laitinen *et al.*$^{2)}$ who used at the outset for LiCl-KCl eutectic melt.

The authors tried to apply this method to the molten glass system and calculate the diffusion coefficients of metallic ion. In the present paper sodium borate and silver ion were chosen as the base glass and a metallic ion, respectively. Diffusion coefficients and its activation energy were calculated. Discussions on the structure of melt was tried by comparing these values with those in some molten salts.

§ 2. Theory of chronopotentiometry

When a cathode reaction, $O+ne\rightarrow R$, is carried out under constant current in the solution containing a large excess of supporting electrolyte, and substance O and R are transported only by diffusion, moreover, electrode reaction is reversible, the potential of a working electrode varies with time as shown equation (1)[3].

$$E=E^0+\frac{RT}{nF}ln\frac{f_0D_R^{1/2}}{f_RD_0^{1/2}}+\frac{RT}{nF}ln\frac{C^0-Pt^{1/2}}{Pt^{1/2}} \tag{1}$$

with

$$P=\frac{2i_0}{\pi^{1/2}nFD_0^{1/2}}$$

where, E^0 : standard potential
f : activity coefficient
D : diffusion coefficient
C^0 : bulk concentration of the oxidized substance
i_0 : current density
Subscript O and R mean the oxidized and the reduced substance, respectively.
n : number of electrons involved in electrode process
Others are customary symbols.

The potential calculated from equation (1) is infinite when time, $t^{1/2}$, becomes equal to C^0/P ($\equiv\tau^{1/2}$). τ is called transition time and given by equation (2), so called Sand's equation.

$$\tau^{1/2}=\frac{\pi^{1/2}nFC^0D_0^{1/2}}{2i_0} \tag{2}$$

According to equation (2), the diffusion coefficient of oxidized substance can be calculated when the transition time is measured and the bulk concentration is known. By substituting C^0 in equation (1) by the function of τ derived from equation (2), equation (3) is obtained.

$$E=E_{1/2}+\frac{RT}{nF}ln\frac{\tau^{1/2}-t^{1/2}}{t^{1/2}} \tag{3}$$

with

$$E_{1/2}=E^0+\frac{RT}{nF}ln\frac{f_0D_R^{1/2}}{f_RD_0^{1/2}}$$

Equation (3) is the same form as the equation of a reversible polarographic wave, provided that $\tau^{1/2}$ and $t^{1/2}$ are respectively replaced by limiting current, i_d, and diffusion current, i. Therefore, the polarographic wave analysis is possible and number of electrons in electrode process, n, can be calculated from plots of E *vs.* $ln\,(\tau^{1/2}-t^{1/2})/t^{1/2}$. In case that the reduced substance, R, deposits on the working electrode at the state of activity of unity, the relation between potential and time is shown by equation (4).

$$E=E_{1/2}+\frac{RT}{nF}ln\,(\tau^{1/2}-t^{1/2}) \tag{4}$$

Granting that electrode reaction is irreversible, equation (2) can be obtained but the relation between potential and time is transformed into equation (5).

$$E=E_{ir}+\frac{RT}{\alpha nF}ln\left[1-\left(\frac{t}{\tau}\right)^{1/2}\right] \tag{5}$$

with

$$E_{ir}=\frac{RT}{\alpha nF}\;ln\,\frac{nFk^0_{f,h}\,C_0}{i_0}$$

where α : transfer coefficient
$k^0_{f,h}$: rate constant for the reaction, $O+ne\rightarrow R$

Here, as to the suitability mentioned at the beginning of this section the following consideration can be made for $Na_2O\cdot 2B_2O_3$ system containing a little amounts of silver ion : It is said that in Na_2O-B_2O_3 system the mobility of sodium ion nearly equals unity. The ratio of sodium ion to silver ion is about 3×10^3 for $Na_2O\cdot 2B_2O_3$ glass containing 0.029 wt%Ag_2O. From the above fact and the rough equality of mobilities of sodium ion and silver ion in aqueous solution it may be regarded that silver ions in the molten glass do not migrate by the effect of electric field, but transfer only by the diffusion attributing to concentration gradient. Moreover, discharge of silver ion gets far ahead of that of sodium ion in a cathodic process. Accordingly, the normal electrochemical technique can be applied to such kinds of molten glass.

§ 3. Experimental procedure

3.1 preparation of sample

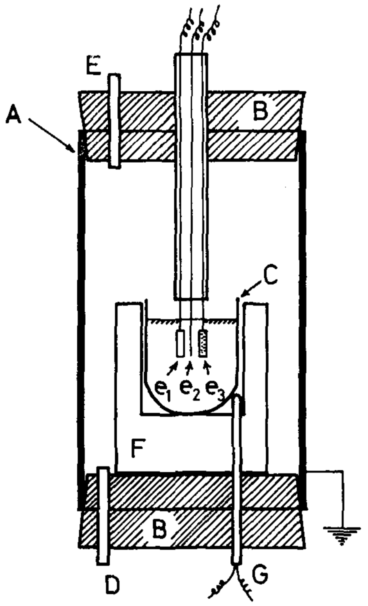
Sodium diborate having comparatively low liquidous temperature (742.5°C) was selected as the base glass by considering that a silver wire was used as a working electrode. The specimen containing a little amounts of silver ion was prepared from sodium carbonate, boric oxide and silver oxide which were of reagent grade and were dried sufficiently. These mixtures were melted at about 950°C in alumina crucible in the air until well refined, then quenched.

3.2 Apparatus

In Fig. 1 is shown schematic diagrams of electrolytic cell. A is a stainless steel tube, which was grounded in order to avoid the induction due to furnace heating elements. The both ends of the tube were plugged by silicone rubber stoppers so that the measuring can be carried under argon stmosphere. Argon gas was purified through pyrogallol solution, conc. H_2SO_4, KOH, and silica gel, in turn. Temperatures were measured by Pt-Pt·Rh thermocouple fixed under the alumina crucible.

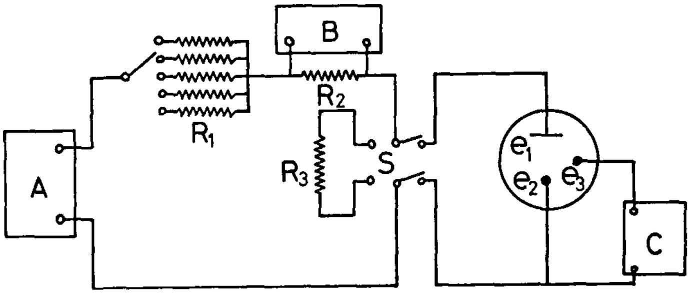
As shown in the figure, the electrolytic cell consists of the alumina crucible, sample glass and three electrodes. A working electrode was made of a silver wire (0.5 mm. in diameter). A rectangular piece of platinum foil of 0.05 mm. thickness and 6.5×13.0 mm. size was used as an auxiliary electrode. As a reference electrode, was prepared the platinum cylinder having pinholes which was filled by a small amount of $Na_2O \cdot 2B_2O_3$ glass containing 0.182 wt%PtO_2, because in argon atmosphere oxygen reaction on platinum electrode can not be expected being different from the case in the air. The metals used as these electrodes were sufficiently polished with very small powder of sodiumbicarbonate in order to make the electrode surface clean. For the working electrode the uniformity of surface area was kept with especial carefullness. Then, the electrodes except the reference one were preserved in the distilled water before use.

In Fig. 2 is shown schematic diagrams of a circuit for chronopotentiometry. In the figure A represents a constant voltage source5) built by



A : Stainless steel tube
B : Silicone rubber stopper
C : Alumina crucible
D : Argon gas inlet
E : Argon gas outlet
F : Crucible-supporter
G : Thermocouple
e_1 : Auxiliary electrode
e_2 : Working electrode
e_3 : Reference electrode

Fig. 1 Chronopotentiometry cell



A : Constant voltage source
B : Potentiometer
C : Cathode-ray oscilloscope
R_1: Series of fixed swapping resistance (500K~10MΩ)
R_2: Standard resistance
R_3: Fixed resistance (10Ω)
S : Start switch
e_1 : Auxiliary electrode
e_2 : Working electrode
e_3 : Reference electrode

Fig. 2 Circuit for chronopotentiometry

the authors and capable of giving 100~200V. By adding fixed swapping resistances of 500K ~10MΩ (R_1, in the figure) to this equipment in series, the device was made from which constant currents between 0.4016 mA and 9.211 μA could be obtained. Current values were calculated from the measured value of the potential drop across a standard resistance (R_2) inserted in series in the circuit by means of a potentiometer (B).

The potential change of the working electrode against the reference electrode with time during electrolysis with constant current was followed by a cathode-ray oscilloscope.

3.3 Experimental procedure

The alumina crucible containing the sample glass was placed in the stainless steel tube. After the furnace was heated at a temperature of 40 to 50°C higher than the liquidous temperature of this glass, the electrodes were inserted with about 1.5cm. depth into the melt. The spontaneous potential of the working electrode against the reference electrode was measured with a pen recorder (input impedence is 2M Ω). After a steady state was obtained, a series of runs of the current-controlled electrolysis on which the silver electrode acted as a cathode were started at the various constant currents and temperatures. The current values were chosen so that the transition times were in the range between 5 and 0.4sec. in order to avoid the influence of a convection and a condenser current whose details would be explained in the next chapter. The surface area of the working electrode which is necessary for calcuration of current density was calculated geometrically by measuring the immersed length of the electrode.

§ 4. Experimental results and Discussion

4.1 Stability of the reference electrode

When two identical electrodes made of the pin-holed platinum cylinders containing ($Na_2O \cdot 2B_2O_3 + 0.182$wt% PtO_2) glass were immersed simultaneously in $Na_2O \cdot 2B_2O_3$ melt at 960°C under argon atmosphere, the variation of the potential difference against time between these electrodes was shown in Fig. 3. The potential difference was considerably rapidly stabilized (<3hrs.) at a value lower than 10mV.

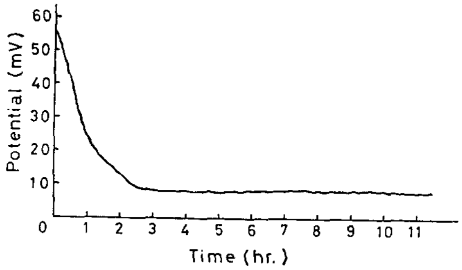
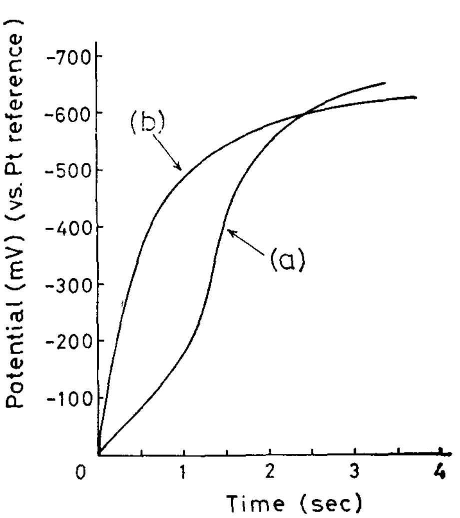


Fig. 3 Stability of electrode potential in $Na_2O \cdot 2B_2O_3$ at 960°C in argon atmosphere

From the result, this electrode is considered to be able to be used as a reference electrode in argon atmosphere.

4.2 Analysis of potential-time curve

In Fig. 4 are shown two typical chronopotentiograms. (a) and (b) correspond to those of



(a) 0.0296/wt%Ag_2O, i_0: 5.004×10^{-4}A/cm^2, 810°C

(b) Supporting electrolyte ($Na_2O \cdot 2B_2O_3$) i_0: 9.058×10^{-4}A/cm^2, 900°C

Fig. 4 Typical chronopotentiograms obtained

$Na_2O \cdot 2B_2O_3$ containing 0.0296 wt%Ag_2O and $Na_2O \cdot 2B_2O_3$ only, respectively. The transition time was determined in Fig. 4 (a) by measuring the time from a beginning of electrolysis to a inflection point. The chronopotentiogram of the supporting electrolyte, $Na_2O \cdot 2B_2O_3$, in Fig. 4 (b) showed monotonic increase and finally reached a constant value.

Table 1. is a set of 6 successive determinations of the transition time of $Na_2O \cdot 2B_2O_3$ containing 0.152wt%Ag_2O. The data of this

Table 1. Precision of Transition Time Measurements (Ag_2O : 0.152 wt%, Current density : 1.087×10^{-3} A/cm^2, Temperature : 882°C)

Run No.	τ (sec.)	$\tau^{1/2}$ (sec.$^{1/2}$)
1	8.03	2.83
2	8.40	2.90
3	8.57	2.93
4	8.93	2.99
5	8.20	2.86
6	8.03	2.83
Average	8.36	2.89
std. dev.	±0.231	+0.043
relative std. dev.	±2.76%	+1.49%

table show that the square root of the transition time was determined with a relative standard deviation of ±1.5%.

At the same time, the experiments were tried in the air by using a platinum wire or a silver wire as the working electrode, but inflection points on potential-time curves were not so notable in both cases as those in argon atmosphere. These facts are cnosidered as being dependent upon the activity change in the process of deposition on the platinum electrode and a little oxidation of silver, respectively. From these facts, all experiments were carried out in argon atmosphere by using a silver wire as the working electrode.

In Fig. 5 are shown the plots of potential-time relations made according to eq. (3) and (4). The plot of potential *vs. log* $(\tau^{1/2}-t^{1/2})/t^{1/2}$ did not yield a straight line but the plot *vs. log* $(\tau^{1/2}-t^{1/2})$ showed a straight line. The number of electrons, n, calculated from the slope of this straight line was equal to 0.94 (neary equal to unity). These facts can be believed to show that the reduction process of silver ion is nearly reversible and the ion is reduced into a metallic state.

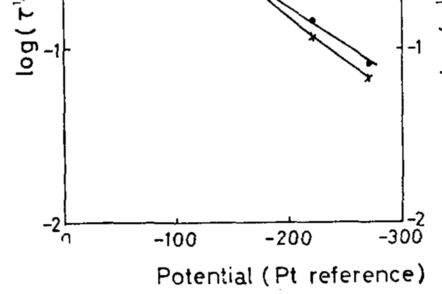


Fig. 5 Plots of $log(\tau^{1/2}-t^{1/2})$ and $log(\tau^{1/2}-t^{1/2})/t^{1/2}$ against potential

4.3 Calculations and considerations of diffusion coefficients

Fig. 6 shows the plots of square root of transition time, $\tau^{1/2}$, against reciprocal of current density, $1/i_0$, on 0.0296wt%Ag_2O as an example, at various temperatures. These plots yielded a set of considerably good straight lines which gather at the origin. This means that Sand's equation comes into existence in the present case, that is, silver ions are transported only by linear diffusion. The slope of these straight lines corresponds to $\pi^{1/2}nFC^0D_0^{1/2}$ (cf. eq. (2)).

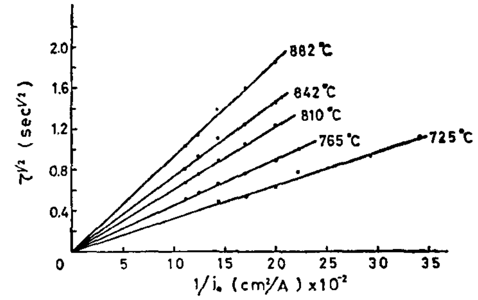


Fig. 6 Plots of $\tau^{1/2}$ *vs.* $1/i_0$ at various temperatures Ag_2O : 0.02961wt%

In this place, the spectral absorptions of the specimens containing 0.152 and 0.0296wt% Ag_2O and of the base glass were measured, in order to examine the state of existence of Ag_2O in $Na_2O \cdot 2B_2O_3$ glass. A very small absorption band whose wave-length is 410 mμ was observed on 0.152wt%, but the specimen containing 0.0296wt% did not show this peak in the same way of the base glass. This absorption band is due to silver colloid⁶⁾. From the above fact, it may be deduced that the specimen containing silver oxide of 0.0296wt% does not contain metallic colloid of silver. Accordingly, diffusion coefficients were calculated by using the analytical concentration of silver ion as the bulk concentration, C^0. The exchange of weight percent into molarity was carried out with the help of the density data measured by L. Shatsis *et al.*[7], in disregard of the effect of addition of silver oxide. In several experiments in the argon atmosphere, the thin layer of silver was occasionally observed around platinum electrodes and on the glass surface but the correction was not carried out because of its very small amount.

In Fig. 7, diffusion coefficients corresponding to two concentrations were plotted against the reciprocal of absolute temperature. Both show the good straight lines, so that Arrhenius equation for diffusion, $D=A\ exp\ (-E/RT)$ comes into existence in these temperature ranges. The calculated activation energies of diffusion were 32.2 Kcal/mol and 31.2 Kcal/mol for 0.0296 wt%Ag_2O and 0.04306wt%Ag_2O, respectively. Diffusion coefficients at same temperature between two glasses of different concentrations differ each other, namely the one having the low Ag_2O content indicates the diffusion constant value as large as four times of the other. This discrepancy is considered to be attributed to the inaccuracy for measurements of the area of electrode surface and the deposition of silver colloid.

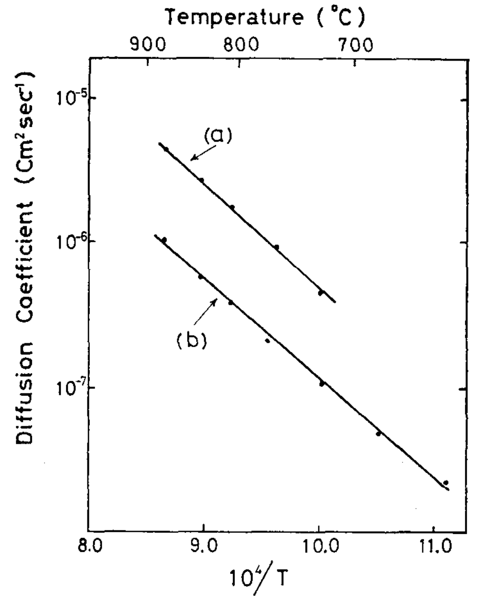


Fig. 7 Diffusion coefficients at various temperatures
(a) 0.02961wt%Ag_2O
(b) 0.04306wt%Ag_2O

The diffusion coefficients at liquidous temperature (742.5°C), 6.5×10^{-7} cm²/sec and 2.1×10^{-7}cm²/sec for 0.0296 wt% and 0.04306wt% Ag_2O, respectively, are considerably smaller in comparison with the value of silver ion, 2.6×10^{-5} cm²/sec, at melting point in LiCl-KCl electic melt measured by Laitinen *et al.*[2] by means of the same technipue, and 1.4×10^{-5} cm²/sec at melting point in 80 KNO_3-20 $LiNO_3$ (mol%) measured by Kawamura[8]. On the other hand, the values of activation energy are considerably larger than the value after Kawamura, 3.1 Kcal/mol[8] and 9.3 Kcal/mol obtained by Ishii *et al.*[9] in strong phosphoric acid. From these facts and the large viscosity coefficient of $Na_2O\cdot2B_2O_3$ melt, about 20 poise* at liquidous temperature, it can be said that considerably large borate anions exist in the molten glass, which make diffusion of silver ion more difficult than that in the other molten salts.

According to H. Eyring *et al.*[10], the diffusion coefficient is expressed in equation (6)

$$D/T=e\lambda^2(k/h)exp\,(\Delta S^{\ddagger}/R)exp(-E/RT) \tag{6}$$

where, λ : the distance between two equilibrium positions
k : Boltzman's constant
h : Planck's constant
$\Delta S^{\ddagger}$: activated entropy for diffusion
E : the observed activation energy for diffusion derived from the equation $D=A\ exp(-E/RT)$
Others are customary symbols.

By using the value of activation energy mentioned above, the term, $\lambda\{exp(\Delta S^{\ddagger}/R)\}^{1/2}$, was calculated from equation (6) at various temperatures. These values for 0.0296 and 0.04306 wt%Ag_2O were, respectively, about 30Å and 15Å almost independently of the temperatures. These values are much larger in comparison with 1.4 and 0.61Å, which were obtained for the self diffusion of phenol in benzene[10] and the diffusion of zinc ion in NaCl·KCl eutectic melt[11], respectively. Provided that the activation entropy, $\Delta S^{\ddagger}$, can be considered not to differ markedly from zero in the same way both for the diffusion of phenol molecule and zinc ion, $\lambda\{exp(\Delta S^{\ddagger}/R)\}^{1/2}$, corresponds to the distance between two equilibrium positions, λ, whose value was several decads in Å in this case as indicated above. This value is believed

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* the value measured by authors by means of a counterbalanced-sphere method

to give a information for the size of borate anion.

On the other hand, the radius of silver ion calculated from Stokes-Einstein's equation (7) in two concentrations at two temperatures scattered between 4.1×10^{-2}Å and 1.9×10^{-1}Å.

$$D=\frac{kT}{6\pi r\eta} \tag{7}$$

where, k : Boltzman's contant
r : radius of diffnsing molecules
η : viscosity coefficient of the medium

These values correspond to about 1/24 and 1/6 times of the authorized value, 0.97Å, respectively. This discrepancy can be attributed mainly to the reason that this melt does not satisfy one of the assumptions under which Stokes-Einstein's equation come into existence —the diffusing molecules are very much larger than those of the medium. In the present case silver ions having small radius diffuse in the medium containing large borate anions.

§ 5. Conclusions

The investigations of cathode reaction of silver ion contained in a molten sodium borate at the temperatures from 880°C to 625°C by means of chronopotentiometry were carried out and following results were obtained.

(1) In case that a silver wire was used as a working electrode, the electrode reaction was almost reversible.

(2) On the occasion that a transition time was measured within several seconds, Sand's equation came into existence and the influence of convection and condenser current could be ignored.

(3) Diffusion coefficient of silver ion was the order of 10^{-7}cm^2/sec at liquidous temperature. This value is considerably smaller than that in the other ordinary molten salts. Activation energy was about 32Kcal /mol, which is much larger than that in the some molten salts.

(4) $\lambda\{exp(\Delta S^{\ddagger}/R)\}^{1/2}$ was the order of several decads in Å, which suggests the existence of large borate anions.

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