Effect of Electrolyte pH on CH₄ Adsorption and Desorption Behavior in Electrochemically Modified Lean Coal

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ABSTRACT: Practical application of the electrochemical method for enhancing coalbed methane (CBM) extraction is limited due to the insufficiency of in-depth experimental and theoretical research. Therefore, H₂SO₄, Na₂SO₄, and NaOH electrolytes with different pH values were selected to electrochemically modify lean coals and their CH₄ adsorption and desorption behaviors were tested. The experimental results showed that the amount of CH₄ adsorption decreased after modification using H₂SO₄ and Na₂SO₄ electrolytes, and increased after electrochemical modification using the NaOH electrolyte. The ratio of CH₄ desorption increased from 83.20 to 90.10 and 87.84%, respectively, after electrochemical modification using H₂SO₄ and Na₂SO₄ electrolytes, and decreased to 81.71% after electrochemical modification using the NaOH electrolyte. The pore volume and average pore size increased, and the specific surface area decreased with the decrease of electrolyte pH. Lower pH electrolytes perform better and the mechanism was analyzed by the change of surface energy, surface groups, and pore structures. The work will provide a basis for the reasonable selection of electrolyte pH when using in situ electrochemical methods for enhancing CBM extraction.

1. INTRODUCTION

Coalbed methane (CBM) extraction not only has importance in the current world in need of clean energy supplies, also an important technical means to reduce methane accidents during the coal mining process. However, the occurrence state of methane in coal is mainly the adsorption state, and the methane adsorption capacity is closely related to the surface area of coal. Previous research studies mainly focused on cracking coal seams to accelerate methane extraction like hydraulic fracturing and hydraulic flushing, which often reckon without the influence of O-containing functional groups on CH₄ adsorption characteristics. Besides the specific surface area, O-containing functional groups on the surface of coal and mineral matters (MM) in coal also play a significant role in the adsorption behavior of methane. The adsorption capacity of CH₄ decreased with the increase of O-containing groups. Feng et al. found that the mesostructures of cell cavity pores with non-compact packing of the clay minerals appear to be the primary sites of methane adsorption in coal.

Electrochemical modification can effectively accelerate CH₄ extraction not only by increasing fractures and pores in coal but also by increasing O-containing groups on the anthracite surface. Guo et al. found that the clay minerals and fine coal powders filled in the cracks of coal samples were released by electrolytic reactions and the time to reach CH₄ desorption equilibrium was shortened by 68%. Electrochemical desulfurization (ECDS) technology can remove sulfur by electrochemical oxidation (ECO) or reduction (ECR) of sulfur compounds in fossil fuels. The organic sulfur compound (represented by R-SH) in coal is oxidized in the anode region to form an oxidation product (RSH), and the addition of oxygen to the RSH increased the polarity of the sulfur compound, making it extractable using a polar solvent or using a polar adsorbent. Reduction at the cathode results in the formation of hydrogen sulfide, which can be removed by gas–liquid separation. The increase of O-containing groups on the coal surface after modification was observed by Zhang et al. and Feng et al., and they both found that CH₄ adsorption decreased with increasing O-containing groups.

Electrolyte pH is one of the key factors that affect electrochemical modification, however, the influence of the electrolyte pH on CH₄ adsorption and desorption still needs further research. Currently, the influence of the electrolyte pH on modification effects is mainly related to the electro-osmotic flow and chemical modification. It was reported that CH₄ adsorption decreased after chemical modification using a lower pH (<7) electrolyte. Feng et al. found that after modification of bituminous with H₂SO₄, (NH₄)₂S₂O₈ and

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H$_2$SO$_4$/(NH$_4$)$_2$S$_2$O$_8$, the O-containing groups on the coal surface increased and methane adsorption decreased. It was found by Zhang et al. that H$_2$SO$_4$ and HNO$_3$ acid treatment generates an acidic surface that can reduce CH$_4$ adsorption in coal-based activated carbon. On the contrary, with higher electrolyte pH (>7) CH$_4$ adsorption was reported to increase after chemical modification. Electrochemical modification is proposed because it not only increases acidic groups on the coal surface but also reacts with minerals filled in coal and eventually leads to their migration. The electrolyte pH also has significance in electrokinetic consolidation of soils, Liaki et al. pointed out that aluminum ions were dispersed and migrated when pH was < 5, resulting in soil strengthening. However, since low pH results in an increase in the corrosion rate of the anode, it is desirable to have extremely high pH values.

In conclusion, the effect of electrolyte pH on CH$_4$ adsorption in lean coal by electrochemical modification has not been well explained. In this paper, 0.05 mol/L H$_2$SO$_4$, Na$_2$SO$_4$, and NaOH electrolytes with pH values of 1.0, 7.0, and 12.7 were used to modify lean coal. CH$_4$ adsorption and desorption in lean coal before and after modification were tested. The surface energy, O-containing groups, and pore characteristics were tested and analyzed by the dynamic contact angle, Fourier transform infrared spectroscopy (FTIR), and low-temperature N$_2$ adsorption, besides, the mechanism of modification using different pH values was explained.

2. RESULTS

2.1. CH$_4$ Adsorption Results after Modification. Figure 1 shows the CH$_4$ adsorption results of lean coal samples with

![Figure 1. CH$_4$ adsorption of a lean coal sample after modification using pressure at 293.15 K.](image)

![Figure 2. Changes of Langmuir constants $V_L$ shown in (a) and $P_L$ shown in (b) after electrochemical modification.](image)

![Figure 3. Desorption ratio of CH$_4$ in lean coal samples before and after modification.](image)

![Figure 4. $D$ of lean coal samples before and after modification.](image)

![Figure 5. Relationship between reduction value of surface tension and pressure after electrochemical modification.](image)
four modification programs under different pressures. The CH₄ adsorption testing results were analyzed using the Langmuir isotherm adsorption equation.\(^1\)

\[
V_{ab} = \frac{V_L P}{(P_L + P)}
\]

where \(V_{ab}\) is the amount of adsorbed CH₄, mL/g; \(V_L\) is the maximum amount of adsorbed CH₄, also known as Langmuir volume, which depends on the properties of the adsorbent and adsorbate, mL/g; \(P_L\) is the CH₄ equilibrium pressure of half of the saturated adsorption amount \(V_L\); and \(V_L\) and \(P_L\) are Langmuir constants, whose changes after electrochemical modification are shown in Figure 2.

Figure 1 indicates that after electrochemical modification using H₂SO₄ and Na₂SO₄ electrolytes, CH₄ adsorption of lean coal decreased, and the decrease is H₂SO₄ > Na₂SO₄. However, after electrochemical modification using the NaOH electrolyte, CH₄ adsorption of lean coal increased. Figure 2a shows that the maximum amount of CH₄ adsorption \(V_L\) in raw samples was 30.03 mL/g, which decreased to 23.27 and 26.67 mL/g, respectively, after modification using H₂SO₄ and Na₂SO₄ electrolytes, and increased to 32.79 mL/g after modification using the NaOH electrolyte. Figure 2b shows that the Langmuir constant \(P_L\) for unmodified lean coal was 0.88 MPa, which increased to 1.15 and 1.05 MPa, respectively, after modification using H₂SO₄ and Na₂SO₄ electrolytes, and decreased to 0.8 MPa after modification using the NaOH electrolyte. \(P_L\) can be used to evaluate the affinity of coal to CH₄ and the ability of CH₄ desorption under reservoir pressure.\(^1\)\(^8\),\(^1\)\(^9\) The experimental fitting results show that \(P_L\) increases with lower electrolyte pH, illustrating that CH₄ adsorption becomes more difficult and that desorption is more readily achieved with lower electrolyte pH.

### 2.2. CH₄ Desorption Results after Modification

The results of desorption were expressed by the desorption ratio and can be obtained using eq 2.

\[
\eta = \frac{V_0}{V_{ab}} \times 100
\]

where \(\eta\) is the desorption ratio of CH₄, %; \(V_0\) is the desorption quantity of CH₄ at a certain time, mL/g; and \(V_{ab}\) is the adsorption quantity of CH₄ in the samples when adsorption equilibrium was achieved, mL/g. Figure 3 shows the desorption ratio of CH₄ in lean coal before and after modification. After electrochemical modification, the CH₄ desorption ratio in coal improved from 83.20 to 90.10 and 87.84%, respectively, using H₂SO₄ and Na₂SO₄ electrolytes.

Figure 7. Peak fitting of oxygen-containing functional groups of lean coal samples before and after electrochemical modification.
and reduced to 81.71% using the NaOH electrolyte. When modified using H₂SO₄ and Na₂SO₄ electrolytes, the time of reaching desorption equilibrium reduced from 450.06 to 368.54 and 404.12 min, respectively, using H₂SO₄ and Na₂SO₄ electrolytes, and increased to 536.92 min after electrochemical modification using the NaOH electrolyte.
The diffusion coefficient can be used to reflect the CH₄ desorption capacity of coal.²⁰ The diffusion coefficient is typically calculated using the single-pore constant-coefficient diffusion model and the general equation of the desorption solution is

\[
\frac{Q_t}{Q_\infty} = 1 - 6 \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -\frac{n^2 \pi^2 D}{r_0^2} t \right)
\]

where \(Q_t\) is the cumulative diffusion amount at time \(t\), cm³/g; \(Q_\infty\) is the cumulative diffusion rate at time \(t\); \(D\) is the constant diffusion coefficient, cm²/s; \(r_0\) is the coal radius, cm; \(t\) is time, s; and \(n\) is the number of cumulative additions of \(\sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -\frac{n^2 \pi^2 D}{r_0^2} t \right)\), and the accuracy of eq 3 increases with the increase of \(n\). To conveniently obtain the diffusion coefficient \(D\), scholars often simplify it when \(n = 1\),³¹ then eq 3 becomes

\[
\ln \left( 1 - \frac{Q_t}{Q_\infty} \right) = -\lambda t + A
\]

where \(\lambda = \pi^2 D/r_0^2\) and \(A = \ln(6/\pi^2)\). The symbol \(-\lambda\) denotes the slope of the \(\ln(z - Q_t/Q_\infty)\) line, and \(A\) denotes the intercept of the line and the vertical axis. Figure 4 shows the diffusion coefficient before and after modification, which can be obtained by substituting the data in Figure 4 into eq 4. After modification, \(D\) increased from 7.1 × 10⁻¹⁰ to 14.61 × 10⁻¹⁰ and 10.14 × 10⁻¹⁰ cm²/s, respectively, using H₂SO₄ and Na₂SO₃ electrolytes and decreased to 6.09 × 10⁻¹⁰ cm²/s using the NaOH electrolyte. The increase of \(D\) revealed that the desorption capacity of CH₄ was improved by H₂SO₄ and Na₂SO₃ electrolyte modification; the decrease of \(D\) revealed that the desorption capacity of CH₄ was inhibited by NaOH electrolyte modification.

2.3. Change in the Surface Free Energy after CH₄ Desorption. Surface excess \(\Gamma\) refers to the difference between the methane concentration on the inner surface of coal and that in the coal structure.²¹

\[
\Gamma = \frac{V}{V_0 S}
\]

where \(\Gamma\) is the surface excess, mol/m²; \(V\) is the CH₄ adsorption, L; \(V_0\) is the adsorption volume of CH₄, which under the standard condition is 22.4 L/mol; and \(S\) is the surface area of coal samples, m²/g. When coal samples adsorbed CH₄, the surface tension decreased. According to Gibbs equation

\[
\gamma = \frac{RT}{V_0 S} \int_0^P \frac{dP}{V} \quad \text{and} \quad \gamma = \frac{RT}{V_0 S} \int_0^P \frac{dP}{V} \quad \text{in eq 6 and integrating pressure from 0 to } P, \text{ we can get}
\]

\[
\Delta \gamma = \gamma_0 - \gamma_i = \frac{RT}{V_0 S} \int_0^P \frac{dP}{V} \quad \text{in eq 7, the following results are obtained}
\]

\[
\Delta \gamma = \frac{RT}{V_0 S} \int_0^P \frac{dP}{1 + bP} = \frac{aRT}{V_0 S} \ln(1 + bP)
\]

Equation 8 shows that the surface tension of coal samples depends on the adsorption capacity of CH₄, the surface structure of coal samples, the temperature of the coal—CH₄ adsorption system, and the pressure of CH₄. The reduction of surface free energy of samples after modification can be obtained by eq 8. The calculation results are shown in Figure 5, which indicate that the reduction of surface tension of lean coal decreased after the amount of adsorbed CH₄ increased with the increase of pressure, and the reduction of surface tension decreased after electrochemical modification using H₂SO₄ and Na₂SO₃ electrolytes, and increased by electrochemical modification using the NaOH electrolyte. Zhang et al. also found that the capacity of gas adsorption decreased with the decrease of the surface tension.²²

2.4. Change in Functional Groups after Electrochemical Modification. The FTIR results of lean coal samples before and after modification are shown in Figure 6. A small vibration band appeared near 3800 cm⁻¹, which was attributed to the stretching vibration of NH (−NH₃, −NH₂).²³ At 507 and 1082 cm⁻¹, the peak of the smectite mineral was greatly reduced. Clay minerals that contain smaller mesostructures than coal adsorbed more methane than coal, and the telocollinite with fewer pores has a lower methane adsorption.

![Figure 10. Change of pore size distribution of lean coal samples before and after electrochemical modification.](image)

Table 1. Pore Characteristics of Lean Coal Samples before and after Electrochemical Modification

| samples | average pore diameter (nm) | <10 nm | 10–100 nm | >100 nm | total | <10 nm | 10–100 nm | >100 nm | total |
|---------|----------------------------|--------|-----------|---------|-------|--------|-----------|---------|-------|
| T1      | 6.942                      | 6.025  | 0.510     | 0.143   | 6.678 | 0.002996| 0.001407 | 0.001746| 0.006149|
| T2      | 8.254                      | 2.713  | 0.183     | 0.075   | 2.971 | 0.004983| 0.000279 | 0.002673| 0.010446|
| T3      | 7.901                      | 3.080  | 0.159     | 0.124   | 3.363 | 0.004048| 0.002536 | 0.002348| 0.008932|
| T4      | 6.601                      | 7.101  | 0.830     | 0.684   | 7.931 | 0.001957| 0.000943 | 0.001349| 0.004249|

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capacity. The reduction in the clay minerals reduced the adsorption of methane, which was consistent with the adsorption test results in Figure 1. The peaks near 876 and 1430 cm⁻¹ were also reduced, which correspond to carbonate minerals. Guo et al. pointed out that this result occurs due to the reaction of acid formed by electrochemical reactions with carbonate minerals.

The zone of 1000–1800 cm⁻¹ provides information on the O-containing groups associated with the C=O stretching vibrations of aromatic rings at around 1600 cm⁻¹. Figure 7 shows the peak fitting results of oxygen-containing functional groups of lean coal samples before and after electrochemical modification. It can be seen that the peaks near 1030 cm⁻¹, which are mainly attributed to the stretching vibrations of Si–O or Si–O–C, decreased notably after different modification schemes. The reason was that the mineral materials such as kaolinite and montmorillonite would be dissolved during the electrolysis reaction. The peaks near 1660 cm⁻¹, which mainly correspond to the acidic groups such as –COOH, obviously increased after modification using H₂SO₄ and Na₂SO₄ electrolytes and slightly decreased after modification using the NaOH electrolyte. Indicating that a lower pH environment was conducive to the increase of acidic groups. Figure 8 shows the peak fitting results of aliphatic structures of lean coal samples before and after electrochemical modification. It can be seen that the peaks near 2920 and 2850 cm⁻¹, which correspond to the vibrations of –CH₂ and –CH₃, respectively, all significantly decreased after different modifications. This phenomenon shows that the alkane side chains of aliphatic structures in lean coal would be broken by acids or bases.

2.5. Change in Pore Structures after Electrochemical Modification. Figure 9 shows the LP-N₂ isothermal adsorption–desorption curves of lean coal samples before and after electrochemical modification. It can be seen that all the isothermal adsorption–desorption curves are type IV, indicating that the adsorption gradually accumulated from the monolayer to multilayer with the increase of pressure, and even capillary condensation occurred at high pressures. All of the hysteresis loops can be classified as type H3 or H4, indicating that the pores of lean coal samples before and after modification are mainly slit pores formed by a lamellar or layered structure. The total adsorption capacity of N₂ increased from 4.12 to 7.25 and 6.19 cm³/g upon modification using H₂SO₄ and Na₂SO₄ electrolytes and decreased to 2.83 cm³/g on modification using the NaOH electrolyte. This phenomenon showed that H⁺ generated by electrochemical reactions and present in the acid electrolyte would enlarge the pores in the lean coal samples, while OH⁻ would reduce the volume of pores.

Figure 10 shows the change of pore size distribution of lean coal samples before and after electrochemical modification. It can be seen that the number of pores with a diameter less than 8 nm notably decreased with a lower electrolyte pH and markedly increased with a higher electrolyte pH. Table 1 shows the changes in pore characteristics including pore size, pore surface area, and pore volume of lean coal samples before and after electrochemical modification. It indicates that the surface area of unmodified coal samples is 6.678 m²/g, which decreased to 2.971 and 3.363 m²/g, respectively, after modification using H₂SO₄ and Na₂SO₄ electrolytes. On the contrary, after electrochemical modification using the NaOH electrolyte the surface area increases to 7.931 m²/g. More adsorption potential is obtained with a larger surface area of the coal sample, resulting in more CH₄ adsorption, as shown in Figure 1. The pore size increased from 6.942 to 8.254 and 7.901 nm, respectively, after modification using H₂SO₄ and Na₂SO₄ electrolytes and decreased to 6.601 nm after modification using the NaOH electrolyte. The total pore volume increased from 0.006149 to 0.010446 and 0.008932 cm³/g after modification using H₂SO₄ and Na₂SO₄ electrolytes and decreased to 0.004249 cm³/g after modified with the NaOH electrolyte. All phenomena illustrated that the larger the pore size, the weaker the binding capacity of methane molecules, and the easier the gas desorption; the change of the pore size verified the desorption results shown in Figure 3.

3. DISCUSSION AND APPLICATION

The use of electrokinetic remediation leads to limited influence of electrolyte solution on groundwater. Sometimes researchers even use electrokinetic remediation to remove underground contaminants. Boulakredeche et al. used electrokinetic remediation with ionic (sodium dodecyl sulfate, SDS) and non-ionic surfactants to remove industrial pollutants like n-hexadecane and anthracene, and found that it is an effective way to decrease the influence of oil production and the petrochemical industry on soil, groundwater, and surrounding ecosystems. As mentioned above, the electrolytes play a catalytic role in the electrochemical modification process and accelerate the electrochemical reactions in a certain time. With the increase of time, ions eventually react and are removed by electrokinetic remediation, which will not affect groundwater. Therefore, electrochemical modification is an environmentally friendly method and has great engineering application prospects.

Moreover, lower pH electrolytes perform better in electrochemical modification. However, on decreasing the electrolyte pH from 7 to 1, the improvement in the effects of electrochemical modification is not ideal. Therefore, based on the economic benefits and equipment corrosion, weak acid or neutral electrolyte was enough for application.

4. CONCLUSIONS

1. The CH₄ adsorption/desorption behaviors in lean coal after modification using electrolytes with different pH values were studied. The changes of surface energy, surface groups, and pore structures were introduced to reveal the modification mechanism.

2. Lower pH electrolyte performs better for decreasing CH₄ adsorption and increasing CH₄ desorption in lean coal by electrochemical modification. Conversely, the electrolyte with a higher pH value makes the CH₄ adsorption/desorption behaviors in the lean coal conducive to enhanced CBM extraction.

3. After modification using electrolytes with lower pH values, the reduction of the surface tension of lean coal samples increased, the O-containing groups increased, and the alkane side chains and minerals decreased, which lead to the inhibition of CH₄ adsorption and the promotion of CH₄ desorption. Besides, the increase of the average pore diameter and pore volume and the decrease of pore surface area can also reflect this phenomenon.

4. The findings in this paper will provide a basis for in situ enhanced CBM extraction by the electrochemical
method. In the future, more modification experiments using electrolytes of various pH values will be performed to explain the modification mechanism of all electrolytic pH values.

5. EXPERIMENTS

5.1. Coal Samples. The test lean coal samples were obtained from Donggu coal mine, Shanxi Province, where a high amount of methane was adsorbed in the coal seam. The coal samples were sealed with plastic bags in the mining working face and sent to a laboratory in the Taiyuan University of Technology as soon as possible to avoid the petrophysical-chemical change caused by oxidation. The mean maximum vitrinite reflectance ($R_{\text{max}}$), the maceral composition of the coal samples, proximate analysis (including moisture, ash, and volatile matter content), and the mineral composition analysis were carried out following the standards GB/T 6948-2008, GB/T 8899-2013, GB/T 212-2008, and MT/T 1086-2008, respectively. The results are listed in Tables 2 and 3.

5.2. Experimental Apparatus. The prepared coal samples were modified in the device, as shown in Figure 11. The device is mainly composed of an electrolyzer, a direct current (DC) power supply, an ammeter, two electrode plates, and several potential probes. The electrolyzer is made of thick Plexiglas plates, their inner dimensions are 110 mm length, 60 mm width, and 80 mm height; the electrolytes selected are 0.05 mol/L H$_2$SO$_4$, Na$_2$SO$_4$, and NaOH electrolytes with 1.0, 7.0, and 12.7 pH values. The DC power was supplied by a DH1722A-2 produced by Dahua Radio Instrument Factory, the output voltage range was 0–110 V and the output current was 0–3 A. The multimeter used was the PeakMeter 18 produced by PEAK METER Intelligent Instruments, China. The probe was a copper probe with good conductivity to monitor the potential changes in different regions during the electrochemical process.

5.3. Experimental Process. T1, T2, T3, and T4 represent unmodified coal samples and samples modified using H$_2$SO$_4$, Na$_2$SO$_4$, and NaOH electrolytes, respectively, as shown in Table 4. According to GB/19560-2008, before modification, the coal samples were processed into fine particles of 0.18–0.25 mm and dried in a vacuum oven at 373.25 ± 2.5 K until a constant weight was achieved. Then, the coal samples were sufficiently saturated in solution with a concentration of 0.05 mol/L, the potential gradient was set to 4 V/cm and the modification time was 120 h.

After the lean sample was fully saturated in the electrolyte, it was placed in an electrolytic cell in the device, as shown in Figure 9 to perform the modification experiment. After modification, the 3H-2000PHD high-pressure gas adsorption and desorption rate analyzer produced by Beishide Instrument Technology was used to test the CH$_4$ adsorption and desorption ratio. The coal adsorption test was carried out by setting the maximum adsorption pressure to 7 MPa at 293.15 K. The CH$_4$ desorption of the coal samples after adsorption equilibrium was tested, and the gas desorption rate at higher than 0.0 mL/min was calculated. A Nicolet iS5 FTIR instrument (Thermo Fisher) was used to investigate the distribution of the functional group of the unmodified and electrochemically modified lean coal samples. The collected spectral range of the instrument is 400–4000 cm$^{-1}$. Before the test, fine coal samples and potassium bromide (KBr) were tableted in a ratio of 1:150 wt %. The average pore size, pore volume, and surface area of the coal samples before and after

| Table 2. Petrological Characteristics and Proximate Analysis of Lean Coal Samples |
|------------------|------------------|------------------|------------------|
| $R_{\text{max}}$ (%) | moisture | ash yield | volatile matter |
|------------------|------------------|------------------|------------------|
| 1.88             | 0.98             | 21.29            | 16.16            |
| 90.32            | 4.29             | 2.12             | 1.36             |

| Table 3. Test Results of Chemical Composition of Lean Coal Samples |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| SiO$_2$ | Al$_2$O$_3$ | CaO | Fe$_2$O$_3$ | SO$_3$ | MgO | TiO$_2$ | Na$_2$O | P$_2$O$_5$ |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| 31.75            | 27.37            | 12.38            | 18.00            | 6.14             | 0.74             | 0.42             | 0.06             | 0.04             |

Figure 11. Schematic of the electrochemical modification device.
electrochemical modification were tested using a specific surface area measuring instrument (American Mike ASAP2020HD88).

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**Notes**

The authors declare no competing financial interest.

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