Study on the Electrical Control Mechanism of Gas Occurrence in a Microscale Coal Matrix

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1. INTRODUCTION

Coalbed methane (CBM), as a crucial unconventional energy source, has attracted increasing attention globally with the continuous adjustment in the world’s energy structure. During the CBM extraction process, the gases are adsorbed mainly in the unique dual pore—fracture system and the matrix of the coal reservoir, restricting the CBM transport and the macroscopic performance of the microscale gas occurrence mechanism using electrical properties. The study reveals the following: (1) the coal reservoirs exhibit a weak negative potential at the nanoscale, and the trends of surface potential (SP) and surface electrical charging density (SECD) are fluctuated with the degree of coal rank increases; (2) there is a good correlation between the SP, SECD values, and the relative content of functional groups; and (3) the charge density on the coal’s microscopic surface influences their gas molecule attraction capacity, affecting the gas adsorption capacity of coal reservoirs at the macroscale. This study presents a theoretical foundation for establishing the molecular force field superposition mechanism of gas occurrence in microscale coal matrix and has broad application prospects in the macroscale numerical simulation of CBM development.

Therefore, the gas adsorption mechanism should be investigated from an electrical viewpoint. Fourier transform infrared (FTIR) is an excellent analytical method for calculating the relative proportions of the different functional groups in coal. The functional group characteristics in the coal samples with different ranks help determine the pore—fracture structure of the coal as well as the characteristics of the associated fluid distribution and transport. Hao et al. explored the effect of oxygen-containing functional groups on the coal surface during CBM adsorption, revealing that coal samples with a higher number of oxygen-containing functional groups showed poor adsorption characteristics. Zhang et al. used in situ FTIR technology to investigate the changes in methyl and methylene in the low-temperature coal oxidation and divided the process into three stages. Furthermore, Xu et al. showed that the CH4 presence inhibited the coal oxidation and the −CH2 and −CH3 groups showed higher activity in the macrophysical phenomenon that generates free charges. The change in SP with different destruction modes exhibits different patterns. Thus, monitoring the EMR of coal reservoirs can support coal mining safety and provide an early warning of coal mine disasters. From a microscopic perspective, the gas adsorption behavior in coal reservoirs is possibly attributed to the action of microscopic molecular forces on the coal matrix surface, ultimately subjecting to electrical forces between the molecules. Therefore, the gas adsorption mechanism should be investigated from an electrical viewpoint.

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low-temperature oxidation process as the primary reactive groups.

The atomic force microscopy (AFM) is a high-precision characterization instrument that can accurately characterize the surface topography of the coal. Additionally, AFM defines the microscopic electrical properties of coal through different modes, such as SP and SECD. Song et al. used AFM to calculate SP and SECD of coal surface to explore the surface electrical properties of coal and its influencing factors. Using FTIR and AFM studies, He et al. observed that the coal surface exhibits weak negative charge characteristics at the nanoscale, while being electrically neutral at the macroscale, specifically known as the size effect of coal SP.

The electrical characteristics of coal are a crucial physical feature. The electrical properties of coal may affect the adsorption and migration behavior of gas molecules in coal reservoirs because of the interaction forces among molecules of different sizes. Therefore, coal samples of different coal ranks from various regions in China were selected in this study to calculate functional group characteristics using FTIR and determine their macroscopic and microscopic electrical properties. Additionally, the results were integrated with the isothermal adsorption data to explore the CBM adsorption mechanism based on electrical properties.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation and Processing. The experimental coal samples were collected from the following basins in China: the Balikun Basin in Xinjiang, Eastern Ordos Basin, and Qinshui Basin in Shanxi, with metamorphism ranging from 0.66 to 2.04, covering three coal ranks: low, medium, and high. The industrial composition analysis following the GB/T 212-2008 guideline in China is given as follows (Table 1). Table 1 shows that the lignite sample has the highest moisture content. With the increasing \( R_{\text{max}} \), the fixed carbon content of the samples increases, while the volatile content decreases. This phenomenon reflects the continuous condensation of macromolecules and the expulsion of nonorganic elements from coal during coalification. 50 mm × 100 mm columns and 1 cm² smooth flat samples were prepared for microscopic and macroscopic electrical measurements. Additionally, coal samples for isothermal adsorption experiments were ground to 60–80 mesh and dried at 150 °C for 12 h.

2.2. Functional Groups of Coal. FTIR estimated the relative content of each functional group in the coal samples. The FTIR measurements were performed using the conventional KBr pellet method with an AVATAR360 IR spectrometer. The FTIR samples were pretreated via grounding to 60–80 mesh, followed by a typical three-step HCl–HF–HCl procedure to achieve demineralization to avoid any influence of minerals on the experimental results. Finally, the samples were dried in a thermostat at 105 °C for 12 h to remove the influence of free water on the –OH measurements in the samples.

2.3. Macroscopic and Microscopic Electrical Properties of Coal. The electrical properties of coal include macroscopic and microscopic characteristics. The macroscopic characteristics typically involve resistivity and dielectric constant. In this study, the resistivities of the coal samples were measured at 60 different frequencies from 0.1 Hz to 200 kHz. For the microscopic electrical properties of coal, the SP, SECD, and electronegativity of samples were calculated. This study used the Dimension Icon AFM from Bruker Inc. to analyze the morphology and SP of the sample microsurface by estimating the microscopic forces between the probe and the sample surface, as shown in Figure 1. Notably, different microscopic surface information requires specific probes, such as the Kelvin probe (KPFM), to investigate coal samples’ SP.

Figure 1. Schematic of the AFM.

The AFM probe and coal surface interaction comprise polarization and interatomic electrostatic force. However, Song et al. observed that the polarization force can be neglected. Thus, we have considered only the electrostatic force while evaluating the force between the Kelvin probe and the coal surface.

The electrostatic force \( F \) comprises coulombic electrostatic force \( (F_{\text{coul}}) \) and capacitive electrostatic force \( (F_{\text{cap}}) \). For an applied quantitative voltage at the tip of the probe, \( F \) between the probe tip and the surface of the sample can be expressed as follows:

\[
F = F_{\text{coul}} + F_{\text{cap}}
= \frac{1}{2} \frac{dC}{\partial Z} (V_{\text{tip}} - V_{\text{CPD}})^2 - \frac{C_{\text{surf}}}{4\pi\epsilon Z^2} (V_{\text{tip}} - V_{\text{CPD}}) - \frac{q_{\text{surf}}^2}{4\pi\epsilon Z^2}
\]

where \( C \) represents the capacitance between the tip of the probe and the surface of samples; \( V_{\text{tip}} \) represents the voltage on the tip of the probe; \( V_{\text{CPD}} \) represents the contact potential difference; \( q_{\text{surf}} \) is the charge on the surface of samples; \( Z \) represents the distance between the probe tip and the sample surface; \( \epsilon \) represents the dielectric constant.

Similarly, from the KPFM mode of the AFM microscope, the phase displacement \( \Delta \phi \) of the probe on the sample surface can be estimated as follows:

\[
\Delta \phi = \frac{1}{2} \frac{dC}{\partial Z} (V_{\text{tip}} - V_{\text{CPD}})^2 - \frac{C_{\text{surf}}}{4\pi\epsilon Z^2} (V_{\text{tip}} - V_{\text{CPD}}) - \frac{q_{\text{surf}}^2}{4\pi\epsilon Z^2}
\]
\[
\Delta \psi = -\frac{Q}{k} \frac{\partial \mathcal{Z}}{\partial \mathcal{Z}}
\]
\[
= -\frac{Q}{k} \left[ \frac{1}{2} \frac{\partial^2 \mathcal{Z}}{\partial \mathcal{Z}^2} \left( V_{\text{tip}} - V_{\text{CPD}} \right)^2 + \frac{q_{\text{surf}}}{2 \pi \epsilon_0 \mathcal{Z}} \left( \frac{C}{Z} - \frac{1}{2} \frac{\partial C}{\partial \mathcal{Z}} \right) \left( V_{\text{tip}} - V_{\text{CPD}} \right) + \frac{q_{\text{surf}}^2}{2 \pi \epsilon_0 \mathcal{Z}^2} \right]
\]

To simplify this equation, let
\[
A = -\frac{Q}{k} \left[ \frac{1}{2} \frac{\partial^2 \mathcal{Z}}{\partial \mathcal{Z}^2} \right], \quad B = -\frac{Q}{k} \frac{q_{\text{surf}}}{2 \pi \epsilon_0 \mathcal{Z}^2} \left( \frac{C}{Z} - \frac{1}{2} \frac{\partial C}{\partial \mathcal{Z}} \right), \quad C = -\frac{Q}{k} \frac{q_{\text{surf}}^2}{2 \pi \epsilon_0 \mathcal{Z}^2} \left( \frac{C}{Z} - \frac{1}{2} \frac{\partial C}{\partial \mathcal{Z}} \right)
\]

Thus, eq 2 can be rewritten as follows
\[
\Delta \psi = A \left( V_{\text{tip}} - V_{\text{CPD}} \right)^2 + B \left( V_{\text{tip}} - V_{\text{CPD}} \right) + C
\]

After calculating, \( A \), \( B \), and \( C \) can be expressed as follows
\[
A = -\frac{Q}{k} \frac{3 \epsilon_0 \mathcal{Z}^2}{2 k} B = \frac{Q}{k} \frac{3 \epsilon_0 \mathcal{Z}^2}{2 k} \frac{h}{Z^2}, \quad C = \frac{k}{Q} \frac{2 \pi \epsilon_0 \mathcal{Z}}{Z} B^3
\]

Accordingly, the SECD (\( \delta \)) of the coal sample can be evaluated as follows
\[
\delta = \frac{q_{\text{surf}}}{S} = \frac{B \epsilon_0 \mathcal{Z}^2}{A Z}
\]

where \( Z \) represents the distance between the probe tip and the sample surface. Herein, \( Z = 140 \) nm, \( \epsilon_0 \) is the vacuum dielectric constant, and \( \epsilon_1 \) is the relative dielectric constant of the sample.

### 2.4. Adsorption Experiments of Coal Samples

The methane isotherm adsorption experiment strictly follows the GB/T19560-2008 guideline in China. The Langmuir pressure and Langmuir volume of the coal samples were calculated using the volumetric method. The schematic of the experimental apparatus is shown in Figure 2. We calculated the CH\(_4\) adsorption capacity for six coal samples at two different temperatures. Initially, the samples were ground to 60–80 mesh and dried in a thermostat at 105 °C for 12 h before storing in a drying dish for use. The coal samples' adsorption volumes were calculated at eight pressure points for pressures ranging from 0.1 to 13 MPa. Accordingly, the Langmuir volume \( V_L \) and the Langmuir pressure \( P_L \) of the coal samples were calculated.

Previous studies have established the Dubinin–Astakhov (D–A) model as a more suitable equation than the Dubinin–Radushkevich (D–R) model for the isothermal adsorption of coal. Therefore, the D–A equation is used for curve fitting and calculations.

Each time the adsorption process reaches equilibrium, the amount of CH\(_4\) adsorbed (i.e., the amount of CH\(_4\) reduction) satisfies the following condition
\[
PV'' = nZRT
\]

where \( P \) is the adsorption pressure (MPa); \( V'' \) is the volume of free CH\(_4\) (cm\(^3\)); \( n \) is the number of moles of free CH\(_4\); \( Z \) is the compressibility factor; \( R \) is the universal gas, \( R = 8.3144 \) J/(mol·K); and \( T \) is the absolute temperature (K).

According to the Langmuir equation, fitting is the relationship between the CH\(_4\) adsorption volume and pressure according to the Langmuir equation given as follows
\[
V = V_L \frac{V_L P}{P + P_L}
\]

where \( V \) is the CH\(_4\) adsorption volume (cm\(^3\)/g); \( P \) is the adsorption pressure (MPa); \( V_L \) is the Langmuir volume (cm\(^3\)/g); \( P_L \) is the Langmuir pressure (MPa).

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization of Functional Groups in Coal Samples

FTIR revealed the functional group data of the coal samples (Figure 3). The distribution pattern of the IR spectral curves of coal samples is basically the same; however, the location and intensity of the peaks are considerably different, reflecting the complexity of the macromolecular structure of coal. Based on the different characteristic peaks, Figure 3 is divided into four main ranges for analysis: 3600–3000 cm\(^{-1}\) (oxygenated functional groups), 1800–1000 cm\(^{-1}\) (hydroxyl groups), 3000–2700 cm\(^{-1}\) (aliphatic hydrocarbons), while forming hydrogen bonds, modifying the molecular structure of the coal. The spectral range of 3000–2700 cm\(^{-1}\) involves methyl (–CH\(_3\)) and methylene (–CH\(_2\))–, and the methyl content is more than methylene content. The oxygen-containing functional groups in the 1800–1000 cm\(^{-1}\) range include the carbonyl, aldehyde, carboxyl, ester, and quinone groups. Oxygen-containing functional groups can enhance the CBM adsorption capacity of the coal, and their presence could impede the gas flow in the coal, challenger the gas extraction. Furthermore, the higher the content of aromatic hydrocarbons in the range of 900–700 cm\(^{-1}\), the stronger the gas adsorption capacity of coal.

In this case, we calculate the relative content of the main functional groups by fitting the functional groups to the peaks (Table 2).

According to the data given in Table 2, combined with the \( R_{\text{max}} \) of the coal samples measured in the previous experiments, the contents of C=C, C=O, C=O, and –OH functional groups show a good relationship with the degree of coal metamorphism (Figure 4). The C=C, C=O, and \( R_{\text{max}} \) are positively related, while C=O and –OH are inversely related to...
This indicates that with the increasing degree of coal metamorphism, the $-\text{OH}$ bonds in the coal are decreasing, reflecting the decreasing O and H elements and the condensation of the chemical bonds associated with the C elements. This result could be attributed to the expulsion of heterogeneous elements, decreasing volatiles and a relative increase in carbon content in the coal. This sequential expulsion of unstable structures and the preservation of stable structures are reflected at a macroscopic level in the increasing density and reflectivity of coal.

### Table 2. Relative Content of Functional Groups of Various Coal Samples

| coal samples | A(C=C)/% | A(−CH$_3$)/% | A(−CH$_2$)/% | A(C=O)/% | A(C−O)/% | A(−OH)/% |
|--------------|----------|---------------|--------------|----------|----------|----------|
| BLK          | 5.59     | 6.35          | 3.64         | 0.57     | 3.82     | 24.71    |
| LL           | 7.16     | 11.82         | 4.51         | 0.85     | 3.11     | 17.59    |
| ZYGY         | 6.81     | 5.68          | 4.58         | 0.94     | 2.36     | 20.98    |
| ZJD          | 8.46     | 5.47          | 3.91         | 0.86     | 2.54     | 14.67    |
| XK           | 11.37    | 3.92          | 3.85         | 1.87     | 1.95     | 10.81    |
| CC           | 12.85    | 8.42          | 5.16         | 2.03     | 1.69     | 8.82     |

Figure 3. FTIR spectra of six coal samples.

Figure 4. Histogram of the relative content of each functional group in coal samples [(a): variation of C=C with $R_{\text{O,max}}$; (b): variation of C=O with $R_{\text{O,max}}$; (c): variation of C−O with $R_{\text{O,max}}$; (d): variation of $-\text{OH}$ with $R_{\text{O,max}}$].
3.2. Electrical Characteristic Response of Coal Samples.

3.2.1. Macroscopic Electrical Properties. The electrical characteristics of coal comprise macroscopic and microscopic characteristics. The main electrical macroscopic characteristics are resistivity and dielectric constant. In this case, the dielectric constants of the coal column samples and the part of the resistivity values at 60 different frequencies ranging from 0.1 Hz to 200 kHz are given in Table 3 and Figure 5.

Table 3. Resistivity and Dielectric Constant Values of Coal Samples

| coal sample | R/Ω  | ε/×10⁻⁸ |
|-------------|------|----------|
| BLK         | 350,066,000 | 22,757,1000 | 48,698,200 | 10,634,500 | 3,932,300 | 1,247,400 | 378,764 | 37.36762 |
| LL          | 206,640,000 | 132,369,000 | 35,181,100 | 16,654,700 | 7,633,130 | 2,027,190 | 491,831 | 7.01261 |
| ZIGY        | 4,183,190,000 | 865,182,000 | 119,040,000 | 27,174,000 | 10,257,700 | 2,382,010 | 537,291 | 6.41618 |
| ZJD         | 1,243,540,000 | 542,736,000 | 262,705,000 | 127,864,000 | 32,225,500 | 4,685,690 | 565,047 | 6.84812 |
| XK          | 251,962,000 | 144,434,000 | 24,939,300 | 4,218,260 | 1,191,670 | 207,983 | 8.7676 |
| CC          | 3,012,870,000 | 801,557,000 | 280,605,000 | 120,942,000 | 34,425,200 | 5,001,910 | 578,373 | 12.016483 |

Figure 5. Resistivity and dielectric constant of coal samples [(a): variation of resistance with test frequency; (b): variation of ε with R_o,max].

Figure 6. Planar and three-dimensional potential distribution of coal sample BLK under AFM [(a): planar distribution characteristics of SP on sample surface; (b): stereoscopic distribution of SP on the sample surface; (c): the curves of SP values in two cross sections in Figure 6a].

3.2. Electrical Characteristic Response of Coal Samples. Macroscopic Electrical Properties. The electrical characteristics of coal comprise macroscopic and microscopic characteristics. The main electrical macroscopic characteristics are resistivity and dielectric constant. In this case, the dielectric constants of the coal column samples and the part of the resistivity values at 60 different frequencies ranging from 0.1 Hz to 200 kHz are given in Table 3 and Figure 5.
As shown in Table 3 and Figure 5a, the resistivity of the coal samples decreases with the increasing test frequency and quadratically decreases with the logarithm of the frequency. The dielectric constant ($\varepsilon$) of the coal samples first decreases and then increases with increasing $R_{\text{omax}}$ (Figure 5b).

### 3.2.2. Microscopic Electrical Characteristics.

The KPFM mode of the AFM (scanning range = 5 $\mu$m x 5 $\mu$m) is applied to obtain the microscopic SP data of the coal samples. The potential is a fundamental physical quantity describing the electrostatic field properties. Additionally, the microscopic SP parameter characterizes the electrical properties specific to the microscopic surface of coal, referring to the difference in potential value caused by the mobility variation of ions or electrons at the junction of two phases. It describes the molecular arrangement information on the microscopic surface of the coal body. SECD represents the density of charge distribution on the coal surface, referring to the number of charges contained in a unit area.

Figure 6a,b demonstrates a nonuniform SP distribution on the coal surface. The two red and blue cross sections in Figure 6a illustrate the nonuniformity of the potential distribution (Figure 6c); however, after the SP values’ calculation, it shows a good normal distribution characteristic (Figure 7) and a weak negative SP characteristic in general.

The SP values for the different coal samples were calculated as explained in Section 2.3 and are shown in Table 4. With increasing the coal rank, the SP values first increased slightly, reaching a maximum at $R_{\text{omax}} = 1\%$, followed by a decrease with the degree of metamorphism, reaching a minimum of $-43.5$ $\mu$V (Figure 8).

Using of the previous formula (eqs 2–4), the SECD of each coal sample can be estimated, as given in Table 5.

The SECD of the coal samples demonstrates a decreasing trend followed by an increasing trend with increasing coal deterioration, overall exhibiting a good correlation with the SP values (Figure 8). In terms of the correlation between SP, SECD, and the functional groups’ relative content, four functional groups exhibiting a good correlation with coal samples’ SP and SECD values are presented statistically in Figure 9. Figure 9 shows that the change in the relative content of each functional group with changing coal metamorphosis degree is consistent with the variation in SP for the corresponding coal sample. According to the relationship between SECD and the relative content of each functional group (Figure 10), based on the variation in $R_{\text{omax}}$, the relationship between each functional group and the SECD value shows a “U”-shaped trend, signifying an initial decrease followed by an increase. Thus, it indicates that the attraction to electrons of each functional group contributes to the coal samples’ overall SP and SECD values.

In addition to SP and SECD, electronegativity is a parameter representing the microscopic electrical properties of the material surface. Using the relative content of the functional groups obtained previously (Section 3.1) and the electronegativity of each functional group calculated from previous tests (Table 6), the electronegativity of each coal sample can be estimated. Assuming that the electronegativity of each functional group is $X_{G_i}$ per unit and this functional group’s relative content in coal sample is $A_i$, the cumulative electronegativity of a functional group in coal sample can be expressed as follows

$$X_i = A_i \times X_{G_i}$$

Furthermore, the overall electronegativity $X_o$ of a coal sample containing multiple functional groups can be expressed as follows

$$X_o = \sum_{i=1}^{n} (A_i \times X_{G_i})$$

### Table 4. SP of Coal Samples

| coal sample | range of SP/mV | mean value of SP/$\mu$V | $R_{\text{omax}}$/% |
|-------------|----------------|-------------------------|---------------------|
| BLK         | −46−45         | −28.7                   | 0.66                |
| LL          | −53−53         | −19.3                   | 1.07                |
| ZYGY        | −48−47         | −23.4                   | 1.32                |
| ZJD         | −52−49         | −31.7                   | 1.50                |
| XK          | −76−76         | −38.6                   | 1.77                |
| CC          | −148−148       | −43.5                   | 2.04                |

Figure 7. SP values for sample BLK.

Figure 8. Data distribution patterns and fitted curves for SP and SECD.
where $A_i$ represents the spectral peak area of a functional group, the value of which has been calculated in Table 2.

The cumulative electronegativity of each coal sample was evaluated from the identified electronegativity of each main functional group (Table 6).

Figure 11 shows that the contribution of $-\text{OH}$ to the overall electronegativity is the highest, followed by the impact of the $\text{C} = \text{C}$ group. A gradual increase in $R_{o,\text{max}}$ increases the contribution of $\text{C} = \text{C}$ and $\text{C} = \text{O}$ and decreases the $\text{C} - \text{O}$ and $-\text{OH}$ contribution to the cumulative electronegativity of the coal body. A similar trend is observed with an individual functional group content change with increased coalification degree.

### 3.3. Adsorption Characteristics of Coal Samples

The isothermal sorption data for the six coal samples were estimated using the volumetric method and the $D-A$ model (Figure 12). Figure 12 shows that the adsorption capacity for CH$_4$ is reduced with an increase in temperature; however, the variation is different for each coal sample. Specifically, for the low- and medium-rank samples, the variation in adsorption with increased temperature conditions is prominent, up to 19.51% (sample LL). By contrast, the variation in adsorption is relatively insignificant for the high-rank samples, with the lowest variation being 3.3% for the sample CC (Table 7).

For different samples at the same temperature, the CH$_4$ adsorption capacity first decreases, followed by an increase. Sample LL exhibited the lowest adsorption and the most extensive variation in adsorption capacity at different temperatures.

Generally, the medium-rank coal samples had the lowest adsorption capacity (Figure 14) and minor variation with increased pressure to facilitate maximum adsorption. Conversely, the high-rank coal sample showed more substantial adsorption capacity and continued to adsorb CH$_4$ with increased pressure (Figure 13). Notably, the sample LL of low rank exhibited a decrease in overall adsorption at 35 °C as the pressure increased to 10 MPa. At 35 °C, the pore-fracture structure within the sample is believed to change under high...
pressure, causing the desorption of CH$_4$ molecules adsorbed on the coal matrix surface. However, the molecular collisions were insufficient to balance the desorption of the adsorbed CH$_4$ molecules, leading to decreased adsorption. Consequently, it is reasonable to assume that other samples may also exhibit gas desorption behavior at higher temperatures and pressures.

4. DISCUSSION OF THE ADSORPTION BEHAVIOR MECHANISM

4.1. Influence of Coal Microstructure on Electrical Properties. Coals with different metamorphism degrees have varied relative functional group content, which affects their microstructure, resulting in different microscopic SPs of the coal. Figure 4 reveals that as the metamorphism degree increases, the relative content of the coal’s main functional groups, that is, the C=C and C=O increases, whereas that of the C−O and −OH decreases along with a correlation change between the SP and SECD of the coal. Song et al. observed that the functional group C=C in coal is generally present in aromatic rings and side chains. The benzene ring is a basic unit and forms various aromatic rings owing to strong ability of its molecular orbitals to attract electrons. In the case of oxygen-containing functional groups, the oxygen atom is more electronegative than the carbon and hydrogen atoms; thus, it easily attracts electrons. Studies have reported that the shared electron pairs in the oxygen-containing group tend to favor the oxygen atom, leading to stronger polarity. This results in an overall contribution to the SP value of coal.

The ability of each functional group to attract electrons and the change in the relative content of each functional group during the coalification process modifies the SECD value of coal. As illustrated in the previous study (Figure 10), with an increase
in the degree of metamorphism of coal, the macromolecules in coal continue to condense and integrate. Consequently, it increases the C=C and C=O functional group content, which can attract more electrons and decrease the C–O and –OH content, which causes less electron attraction. The aforementioned phenomenon results in an overall SECD, reaching a minimum $R_{\text{p,max}}$ of 1.0−1.2, followed by a continuous increase in SECD. Thus, the variation in the relative content of functional groups in coal samples with different coal metamorphism explains the changes in the corresponding SP and SECD values.

4.2. Effect of Microscopic Electrical Properties on Adsorption Capacity. Generally, considering the attraction of coal surface macromolecules to CH$_4$ molecules, researchers believe that CBM adsorption occurs via the physical adsorption. The molecular force between coal surface and CH$_4$ molecules, the Van der Waals’ force, comprises electrostatic force, London dispersion force, and Debye induction force, which can be expressed as follows:

$$\text{Figure 12. Comparison of adsorption capacity of the same sample at different temperatures [(a): BLK; (b): LL; (c): ZYG; (d): ZJD; (e): XK; (f): CC].}

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|}
\hline
Sample & $R_{\text{p,max}}/\%$ & Adsorption amount of 30 \degree C/cm$^3$/g & Adsorption amount of 35 \degree C/cm$^3$/g \\
\hline
BLK & 0.66 & 23.00055 & 19.79262 \\
LL & 1.07 & 16.17693 & 13.02058 \\
ZYGY & 1.32 & 22.77753 & 20.48787 \\
ZJD & 1.50 & 26.94129 & 25.10841 \\
XK & 1.77 & 30.77825 & 28.54736 \\
CC & 2.04 & 31.97617 & 30.92068 \\
\hline
\end{tabular}
\end{table}
where $E_{K1} + E_{K2}$ is the electrostatic force between the coal surface and CH$_4$ molecules; $E_{D1} + E_{D2}$ is the Debye induction force; $E_L$ is the London dispersion force; $\mu_c$ and $\mu_g$ are the permanent dipole moment of coal and gas molecules; $Q_c$ and $Q_g$ are the quadrupole moment of coal and gas molecules; $r$ is the distance between coal and gas molecules; $T$ is the temperature; $T_c$ and $T_g$ are the polarizability of coal and gas molecules; and $I_c$ and $I_g$ are the ionization of coal and gas molecules.

Macroscopically, the methane from the external environment enters the pore—fracture structure system of the coal reservoir under the concentration difference (Figure 15a,b) and is transported in these spaces. 41-44 The interaction (the Van der Waals’ force) between the molecular electrons in the functional groups (sphere with blue outline) and the CH$_4$ molecules produces intermolecular forces, causing the coal molecules to attract the CH$_4$ molecules. According to the previous results, different functional groups in the same coal sample exhibit different SECD (the dense distribution of blue spheres in Figure 15c) and varied attraction for CH$_4$ molecules. Therefore, different numbers of CH$_4$ molecules possibly gather near different functional groups. Additionally, in the case of coal samples with different coal ranks and different relative functional groups contents, different adsorption capacities for CH$_4$ can be observed. 45

The analytical results obtained using the KPFM mode of the AFM was used to investigate the microscopic electrical characteristics of the surface of the coal samples. First, the SP values varied across the coal surface and were distributed within ±150 mV. However, the values showed good normal distribution characteristics (Figure 7), suggesting a weak negative electrical potential at the nanoscale but being electrically neutral at the macroscale. The aforementioned result could be attributed to the functional groups’ unique ability to attract electrons and the stronger contribution of the C=O and -OH groups to the overall negative potential characteristic than the C=O and -OH groups. Thus, coal’s complex microscopic pore—fracture structure has a certain amount of surface electrons, indicating a weak negative SP characteristic. Furthermore, coal is in contact with the earth’s equipotential surface in its natural environment; therefore, it is electrically neutral at the macroscopic level.

The microscopic SP represents one of the characteristic values of coal surface charges. A stronger negative SP characteristic...
suggests more negative charges on the coal surface, consistent with the calculated SECD characteristics. A good linear relationship between the coal’s SP and SECD values and the gas adsorption is illustrated in Figure 16. Each coal sample’s relative functional group content contributes to the overall SP and SECD values. Although the SP and SECD values do not vary linearly with the increasing coal metamorphism degree, the amount of gas adsorption measured for each test coal sample at the corresponding metamorphism degree exhibits a good linear relationship with the SP and SECD. Specifically, the trend of the SP and SECD values of the coal with \( R_{o,max} \) is consistent with the \( \text{CH}_4 \) adsorption of the coal samples. Thus, it confirms the crucial influence of the microscopic SP and SECD characteristics of the coal on its gas adsorption.

4.3. Effect of Macroscopic Electrical Properties on Adsorption Capacity. Figure 17 demonstrates that increasing the coal metamorphism degree initially showed a decrease, followed by an increase in the dielectric constant \( \varepsilon \) of each sample. This is consistent with the change in adsorption capacity. Notably, the \( \varepsilon \) values of ZJD and XK, located in the middle-rank coal, are low and their adsorption capacity is high. The aforementioned result could be attributed to the performed \( \varepsilon \) measurement on a 50 mm \( \times \) 100 mm column sample (not dried) and adsorption measurements on a 60–80 mesh powder sample. The moisture in the column sample modified the \( \varepsilon \) values, causing a low \( \varepsilon \).

In the case of resistivity testing of coal samples, the resistivity values were higher for the low- and medium-rank coal samples and the high-rank sample CC (Figure 5a). The resistivity test results of the analyzed coal column samples did not correlate efficiently with the adsorption values due to minerals, inorganic matter, moisture, and pore-fracture structure in coal.\(^{46,47}\) However, we can speculate that all the aforementioned factors affect the gas adsorption in coal.

5. CONCLUSIONS

In this study, the relationship between the microscopic and macroscopic electrical characteristics and the microstructure of the coal was analyzed using the FTIR, AFM, and isothermal adsorption experiments. Furthermore, the coal gas adsorption mechanism was explained from the perspective of electrical properties. The specific conclusions drawn are summarized as follows: (1) A nonuniform SP distribution is observed on the coal surface; however, it showed a statistically good normal distribution and a weak negative SP characteristic at the nanoscale; (2) with an increase in the coal rank, the SP values first increased slightly, reaching a maximum value at \( R_{o,max} = 1\% \), followed by a decrease with the metamorphism degree, reaching a minimum value of \(-43.5 \mu\text{V}\). The SECD of the coal samples showed a decreasing trend followed by an increase with increasing coal rank, overall exhibiting a good correlation with the SP values; (3) four functional groups (\( \text{C}==\text{C} \), \( \text{C}==\text{O} \), \( \text{C}−\text{O} \), and \( −\text{OH} \)) correlated with the SP and SECD values of coal samples. The electron attraction of each functional group contributed to the overall SP and SECD values of the coal samples; (4) the microscopic and macroscopic electrical characteristics with different coal ranks showed good agreement with the \( \text{CH}_4 \) adsorption capacity. This study provides a new way of thinking for revealing the mechanism of gas adsorption in coal reservoir and provides potential help for the production and development of CBM.

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