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Characterization of Colloidal Particles using Electrical Impedance Spectroscopy in Two-electrode System with Carbon Probe

Yanlin Zhao[a,]*, Mi Wang[b], Jun Yao[c]

[a]*Department of Thermal Energy Engineering, College of Mechanical and Transportation Engineering, China University of Petroleum (Beijing), Beijing 102249, China*
[b] *Institute of Particle Science and Engineering, School of Process, Environmental and Materials Engineering, University of Leeds, Leeds LS2 9JT, UK*
[c]*School of Energy Research, Xiamen University, Xiamen 361005, China*

Abstract

The colloidal particles have an electrical double layer associated with their surfaces when suspended in an aqueous medium. Under the influence of an alternating electric field, an induced electrical dipole moment can be formed due to the polarization of the electrical double layer. The electrical impedance spectroscopy (EIS) measurement can record the complex impedance, conductivity, relaxation frequency and phase angle caused by the polarization of the electrical double layer. These impedance parameters are in relation to particle characteristics, for example, the particle size. The research about particle size effect on electrical impedance spectra was carried out in a four-electrode system and the result indicated that impedance parameters shows a capability for characterizing the particle size. This paper reports the experimental results from electrical impedance spectroscopy measurements on silica suspensions in a two-electrode system with carbon probe. The main aim is to study the particle size effect on impedance parameters, especially the relaxation frequency and phase angle, to compare the data with those obtained from a four-electrode system with stainless steel electrodes and verify the capability for characterizing colloidal particles in different electrode systems. The particle size effect on the relaxation frequency and impedance phase angle was studied in two different electrode systems and a similar tendency can be observed. It indicates that the capability of impedance parameters for particle characterization is not limited in a four-electrode system, but commonly applicable in different electrode systems.

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* Corresponding author. Tel.:+86-10-87933658; fax:+86-10-87933658.
E-mail address: ylzhao@cup.edu.cn

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1. Introduction

Electrical impedance spectroscopy (EIS) is a powerful technique to investigate the electrokinetic properties of materials and their interfaces [1]. The EIS measurement can be achieved by applying an alternating voltage to the system and measuring the AC current response. If an AC electric field is applied to a particle suspension, a dipole moment can be induced on the particle surface due to the deformation of the electric double layer[2]. The macroscopic display of induced dipole moment is usually represented by the impedance parameters, including the impedance real part, imaginary part, phase angle and the relaxation frequency[3]. These quantities are related to the surface properties of the particles, and therefore can be used to characterize the colloidal particles.

The electrode system which is used in electrical impedance spectroscopy measurement usually includes three different forms: 2-electrode, 3-electrode and 4-electrode systems. In the two-electrode system, two electrodes act as the working electrode (WE) and counter electrode (CE). The two-electrode system is common and easy to use; however the problem of the electrode polarization (electrode-electrolyte interface effects) usually influences the measurements[4]. Three-electrode system involves a third electrode, called reference electrode, which is used to measure the potential of the working electrode. The three-electrode system could be used to investigate the kinetics and mechanism of the electrode reaction occurring on the working electrode surface. In the four-electrode system, two sensor electrodes are involved to measure the AC current response from the suspension. The working electrode (WE) and counter electrode (CE) are used to apply the exciting voltage. Since the functions of electrodes are separated, the electrode polarization effect could be decreased in the four-electrode system[5].

The electrical impedance spectroscopy of silica suspensions have been studied using four-electrode system[6]. However, due to the complex on fabrication and installation, the four-electrode system is not suitable for industrial application. A probe including two-electrode system can be easily put in a vessel in many industrial processes, for example, the batch reaction process, mixing process, and batch crystallization process, therefore, it could have wide application in industries.

In this study, a two-electrode system with carbon probe was proposed and fabricated. The electrical impedance spectra of silica suspensions were measured using this two-electrode probe. The electrical polarization effect was studied and corrected using a constant phase element in the equivalent circuit model. The EIS results were compared with those obtained from four-electrode system. The capability for characterizing colloidal particles by EIS method in different electrode systems was verified.

2. Experimental details

2.1. Experimental setup

Electrical impedance spectroscopy measurements on silica colloidal suspensions were carried out using a two-electrode system with carbon probe as shown in Figure 1. The two-electrode system includes one carbon electrode in the central with surface area of 50.24 mm^2 and a stainless steel electrode with annular shape. The outer shell of the probe was made by stainless steel. The EIS measurement was carried out by applying an alternating excitation voltage (1 volt) with a frequency spectrum from 1 Hz to 32 MHz to the probe. The electrical impedance measurements were taken using a Solartron 1260 Impedance/Gain-Phase Analyzer, with “smart” software.

2.2. Materials

Aqueous silica suspensions with different particle size (12 nm, 18 nm, 35 nm, 70 nm, 220 nm) which were ordered from Fuso Chemical Co., Ltd. Japan were used in EIS measurement. The original samples were firstly diluted to different concentration (10.0wt%, 5.0 wt % *et al.*) using distilled water. Then 4g mixed bed ion exchange resin (Bio-red) was added into 100g diluted suspension. The suspension was stirred overnight (more than 12 hours) by magnetic stirrer at 150 rpm. Finally, the deionized suspensions can be obtained by filtrating the resin using funnel and water pump.

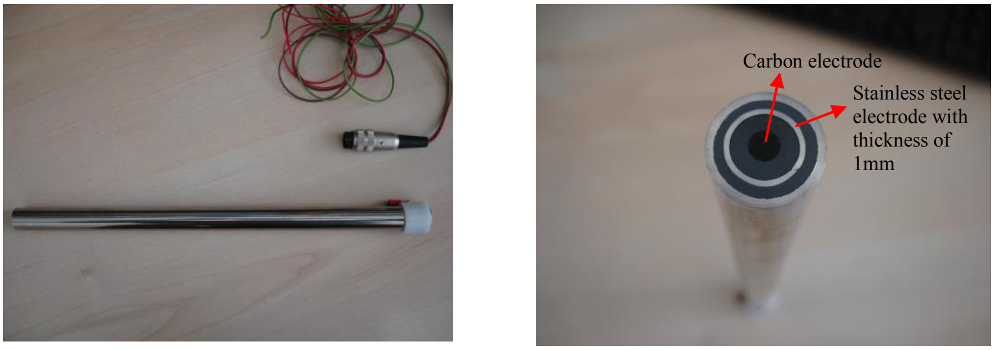


Fig. 1. photographs of the probe with two-electrode sensor.

3. Results and discussion

3.1. EIS of colloidal silica suspensions

The electrical impedance spectra for the silica suspensions (5.0 wt%) measured using two different electrode systems are shown in Figure 2. Two features can be observed in Figure 2(a): several straight lines occurring at low frequency range (1 Hz – 1000Hz) and five suppressed arcs occurring at high frequency range, which shows the dielectric response of the suspensions under the external electric field. The linear section at low frequency ranges results from the electrode polarization (EP) at the surface of plate electrodes. The EP phenomenon occurs due to formation of electric double layer (EDL) capacitances by the free charges that build up at the interface between the electrolyte and the electrode surface. In Figure 2(b), no straight lines can be observed at low frequency range, but only five arcs can be found in the whole frequency range, which means the electrode polarization was decreased significantly in the four-electrode system. The suppressed arc in electrical impedance spectra is a characteristic of dielectric dispersion in the silica suspension, which shows the polarization of charged silica particles under the applied electric field. Over the frequency range of hertz to a few megahertz, the mechanism for an impedance response is the perturbation of charges at the solution-solid interface. Usually, two relaxation mechanisms are: (i) polarization of the counter ions in the diffuse double layer (DDL) on the surface of colloidal particles, (ii) the Maxwell-Wagner (MW) effect that arises from polarization of the large created by contact of two phases with different permittivity [7-8].

3.2. Electrode polarization correction

The electrode polarization contribution to impedance in two-electrode system can be described by a constant phase angle (CPA) element in the equivalent circuit model. The impedance function is given by equation (1):

$$Z^{*}_{\mathrm{CPA}}(\mathrm{T},P)=T(j\omega)^{-P} \tag{1}$$

Where T is a frequency-independent parameter and P is a number between 0 and 1 related to the physical texture of the electrode. For a smooth surface $P = 1$, and for large pores $P = 0.5$ [9].

The electrical impedance spectra measured in two-electrode system can be analyzed using an equivalent circuit model as shown in Figure 3. The complex impedance is given by

$$Z^{*}=Z^{*}_{s}(R_{s})+Z^{*}_{p}(R_{p},C_{p})+Z^{*}_{CPE}(T,P) \tag{2}$$

where, Z_s^* is the solution impedance, Z_P^* is the complex impedance due to the particles and their double layers, Z_{CPE}^* is the complex impedance due to the electrode polarization.

Using the resistance and capacitance in the equivalent circuit to express Z^* yields:

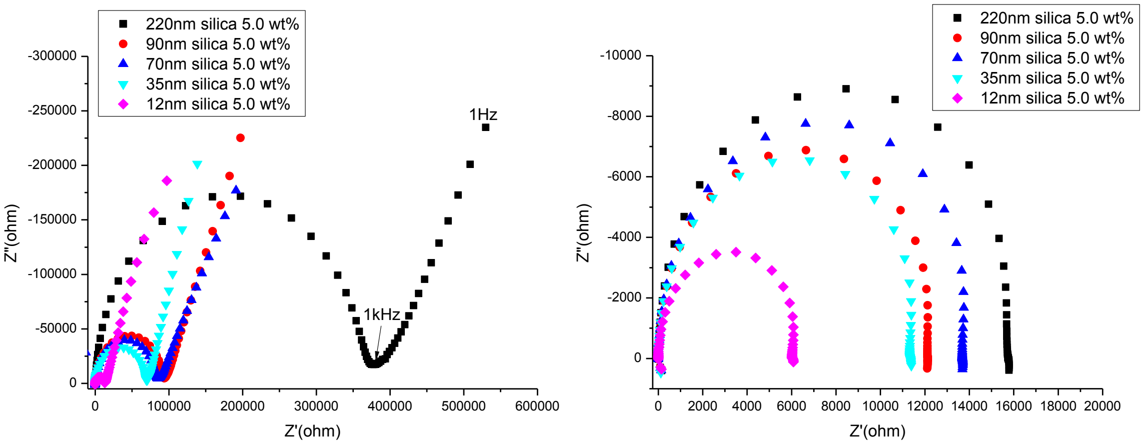
$$Z^* = R_s + \frac{1}{T}(j\omega)^{-P} + \frac{R_p}{1+(\omega R_p C_p)^2} - j\frac{\omega R_p^2 C_p}{1+(\omega R_p C_p)^2} \tag{3}$$

From equation (3), separating real and imaginary parts yields

$$\mathrm{Re}(Z^*) = Z' = R_s + \frac{1}{T}\omega^{-P}\cos(\frac{P\pi}{2}) + \frac{R_p}{1+(\omega R_p C_p)^2} \tag{4}$$

$$\mathrm{Im}(Z^*) = Z'' = -\frac{1}{T}\omega^{-P}\sin(\frac{P\pi}{2}) - \frac{\omega R_p^2 C_p}{1+(\omega R_p C_p)^2} \tag{5}$$

The equation (3) can be used to fit to the experimental data, and obtain the values of T and P. Therefore, the electrode polarization correction can be made by simply removing the Z_{CPE}^* term in the above equations from the experimental impedance data. The fitting result of silica suspension (5.0 wt % with 70 nm particle size) was shown in the Figure 4 (a). It can be seen that the equivalent circuit model fits well and the electrode polarization effect can be eliminated by removing the Z_{CPE}^* term. The correction result after eliminating the electrode polarization effect was showed in Figure 4(b). It can be seen that the EP causes significant effect on the low frequency range (around 1-1000 Hz). For the frequencies higher than 1000 Hz, the EP effect can be neglected.



(a) (b)

Fig. 2. electrical impedance spectra for silica suspensions (5.0 wt %) with different particle size measured using (a) two-electrode system, and (b) four-electrode system

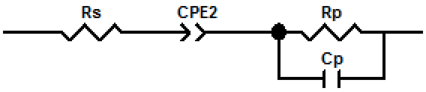
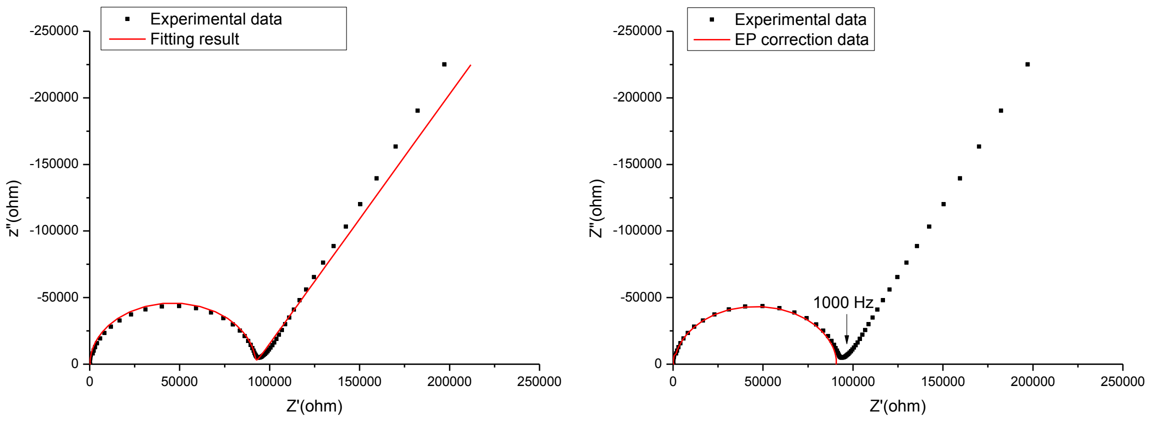


Fig. 3. the equivalent circuit for EIS measurement in two-electrode system



(a) (b)

Fig. 4. electrical impedance spectra for silica suspensions (5.0 wt %, 70 nm) measured using two-electrode system: (a) fitting result using equivalent circuit; (b) the correction data after eliminating the electrode polarization effect.

3.3. Particle size dependence of relaxation frequency and phase angle

The effect of particle size on EIS was studied in colloidal silica suspensions with concentration of 5.0 wt %. The experimental results of the electrical impedance spectra measured using two-electrode system for the colloidal silica suspensions with various particle sizes (12 nm, 18 nm, 35 nm, 70 nm, 220 nm) are showed in Figure 5.

The relaxation due to the polarization of the counter ions in the diffuse double layer (DDL) on the surface of colloidal particles usually occurs at the kHz range. From Schwartz's study [10], the relaxation frequency is related with the path length for the movement of the ion swarm, as shown by the equation:

$$f_{\text{relaxation}} \approx \frac{2D}{a^2} \tag{6}$$

where, *a* is the particle radius, and D is the diffusion coefficient of the counter ions.

From Figure 5 (a), it can be found that the relaxation frequencies, obtained from the peak position on the plots of impedance imaginary parts, decrease with increasing particle size. From Figure 5(b), it can be observed that at a fixed frequency (for example 80 kHz), the absolute values of the phase angle increase with increasing particle size. It can be also noticed that at the MHz range, a relaxation occurs, evidenced by the beginning of an upturned curve at about 4MHz in Figure 5(b). This relaxation is due to the Maxwell-Wagner (MW) effect.

In order to compare EIS measurement using different electrode systems, the particle size effect on the relaxation frequency and impedance phase angle was studied using two-electrode system and four-electrode system and the results are shown in Figure 6 and Figure 7. From Figure 6, it can be found that the relaxation frequencies change inversely with the square of the particle size according to equation (6) in both two-electrode and four-electrode systems. The intercept and slope obtained by linear fitting results are different in different electrode systems. The possible reason could be the different materials which were used in the fabrication of electrode system and the different dimensions of electrodes. In addition, it can be noticed that deviation exists between the experimental data and the linear fitting results based on equation (6). The main possible reason could be the unexpected aggregation of the colloidal particles in suspensions. The silica suspensions which are tested in our experiments are not mono-dispersed samples, and may have aggregation especially when the particle size becomes smaller. From Figure 7, it can be found that the absolute values of impedance phase angle increase with increasing the particle size in both two-electrode and four-electrode systems, which is very clear at 80 kHz. The possible reasons is that the time need in the diffusion process increases with particle radius, and therefore the induced dipole moment lags behind the change of applied electric field to cause a large phase angle shift. The line in Figure 7 is just for the connection between two points without any other meanings. The changing of impedance phase angle with particle size shows a similar tendency in two-electrode system and four-electrode system. However, the experimental data measured in the same suspensions using different electrode system are different, which might be caused by the different material and dimensions of the electrode.

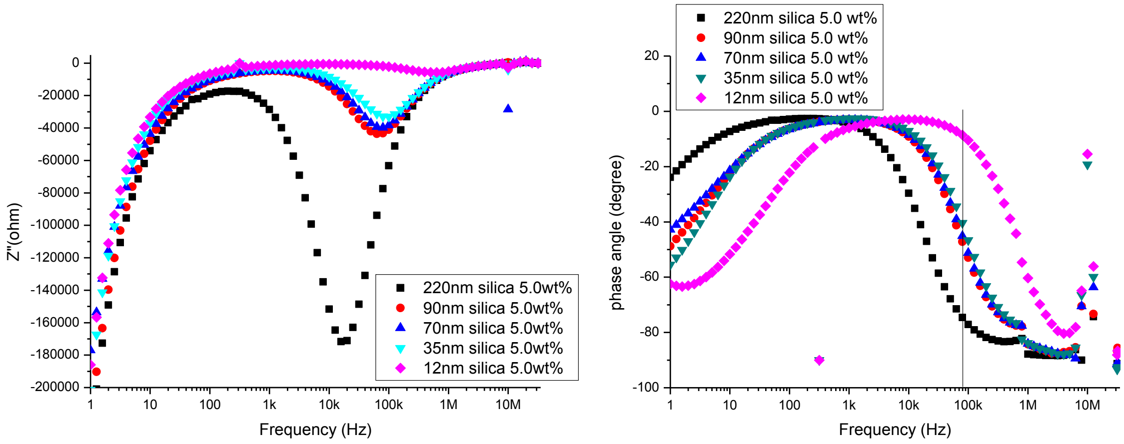
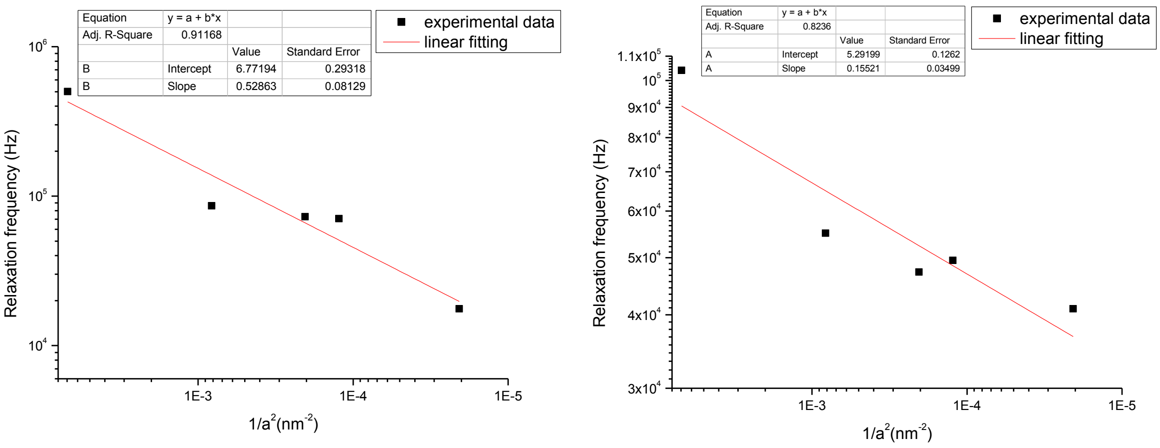


Fig. 5. electrical impedance spectra for silica suspensions (5.0 wt %) with different particle size measured using two-electrode system: (a) impedance imaginary part vs. frequency; (b) phase angle vs. frequency



(a) (b)

Fig .6. the relaxation frequencies change as function of $1/a^2$ (a is the particle diameter): (a) two-electrode system; (b) four-electrode system.

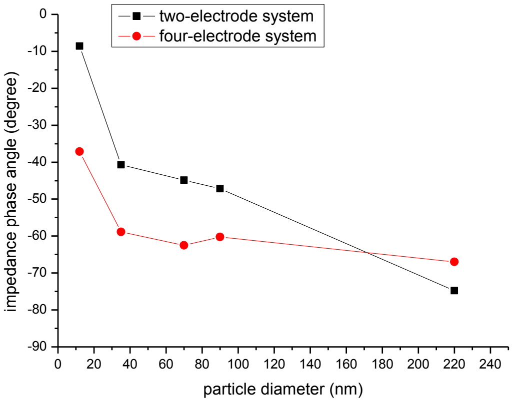


Fig. 7. impedance phase angles at 80 kHz change as function of particle size for silica suspensions (5.0 wt %) measured in two-electrode and four-electrode systems respectively.

4. Conclusions

Electrical impedance spectra of silica suspensions were measured using a two-electrode system with carbon probe. Several straight lines can be observed at low frequency range (1 Hz- 1000Hz), which is the feature of electrode polarization effect. For impedance spectra measured using a four-electrode system, the electrode polarization effect can't be observed even though at low frequency range. The electrode polarization can be simulated by a constant phase angle (CPA) element and be corrected by removing the Z_{CPE}^{*} term from the total complex impedance. The particle size effect on the relaxation frequency and impedance phase angle was studied in two different electrode systems and a similar tendency can be observed. It indicates that the capability of impedance parameters for particle characterization is not limited in a four-electrode system, but commonly applicable in different electrode systems.

Acknowledgements

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