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Measurement of Particle Size Distribution in nano Colloidal dispersions Using Electrochemical Impedance Spectroscopy

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***Abstract*—Electrochemical impedance spectroscopy, as a method for characterizing the impedance properties of materials, can be used to evaluate relative changes in particle size in nano-colloidal dispersions. By applying ultrasonic agitation for varying duration, we induce changes in particle size distribution, then measure the EIS response, including impedance magnitude and phase. The results are compared with dynamic light scattering data to validate the EIS measurements. The approach allows real-time monitoring and minimal sample handling, providing a cost-effective solution for assessing nanoparticle size distribution. This technique has potential applications in industrial processes, food, and biomedical sciences.**

Keywords: Electrochemical Impedance Spectroscopy, particle size, nano-colloidal dispersions

I. Introduction

Colloidal dispersions of nanoparticles play a significant role in fields such as electronics, catalysis, and biomedical sciences. Therefore, characterizing and monitoring the size distribution of nanoparticles is crucial for understanding and utilizing these colloidal systems.

Electrochemical Impedance Spectroscopy (EIS) has emerged as a promising alternative for characterizing the size distribution of nanoparticle in colloidal dispersion [1]. EIS is a non-destructive, label-free, and sensitive technique that can probe the electrical properties of colloidal systems by applying an alternating current (AC) signal over a wide frequency range. The resulting impedance response is influenced by various factors, including the size, shape, and surface characteristics of the nanoparticles, as well as the properties of the surrounding medium [2].

In this study, we propose a method to measure relative changes in the size distribution of a silica nanoparticle colloidal dispersion using EIS. A custom-built pump circulation system. By subjecting the colloidal dispersions to ultrasonic vibration for varying duration, changes in particle size distribution are induced. We monitor the EIS response, including impedance magnitude and phase, and correlate it with the size distribution obtained from complementary dynamic light scattering.

II. Experimental Details

A. Materials

To prepare the silica nanoparticle colloidal dispersions, silica powder from US Research Nano-materials, Inc. was utilized as the base material. The powder's particle size was quoted from the manufacturer at being 60 to 70 nm, with over 99% of the composition being silica, and the remainder consisting of metal ions. The quoted specific surface area was 70 g/mˆ2, and the particles were spherical, minimizing shape-related impact on EIS characterization. The silica powder was diluted in ultra-pure water to create colloidal dispersions of varying concentrations (0.5%wt, 0.4%wt, 0.3%wt, 0.2%wt, 0.1%wt). To mitigate the effects of metal ions on EIS measurements, mixed-bed ion-exchange resin (Bio-Rad) was used to deionize the dispersions, thereby reducing metallic ion interference.

Given that the initial silica particles could aggregate when combined with ultra-pure water without agitation, the manufacturer's reported particle size might not have been reliable. To assess the particle size distribution (PSD) in the colloidal dispersions at different agitation times, the ZetaSizer was employed. Additionally, the colloidal dispersion's pH values were measured using a pH meter (MP225), with conductivity and zeta potential measurements also taken to assess dispersion characteristics.

B. Experiment setup for the EIS Pump Circulation System

To measure relative changes in particle size in a relatively enclosed environment within a colloidal dispersion, a pump circulation system equipped with a four-electrode sensor was used for the experimental measurements. The pivotal element of this system was the Masterflex C/L Dual-Channel Variable-Speed Peristaltic Tubing Pump (model 77120-52) from Cole-Parmer. It comprised stainless-steel tubing with an internal diameter of 1.01 mm and an external diameter of 2.41 mm. A four-electrode sensor was mounted on the right side of the system, consisting of two stainless steel tubes as the working and counter electrodes and two stainless steel needles as reference electrodes. The tubes measured 20 mm in length, with an external diameter of 15 mm and an internal diameter of 13 mm, interconnected by transparent plastic tubing with an internal diameter of 15 mm. The needle electrodes were each 15 mm in length and were positioned to minimize conductivity interference, maintaining a 2 mm distance from the tube electrodes. Adapter connectors were employed to integrate the four-electrode system with the stainless-steel tubing circuit.

When particles were diluted in ultra-pure water to form a colloidal dispersion, they often aggregated, resulting in a larger effective particle size than anticipated. To evaluate relative changes in particle size within the same colloidal dispersion, an ultrasonic bath was incorporated. A Fisher Scientific ultrasonic bath was situated at the inlet point on the right side of the pump circulation system, providing controlled agitation to the beakers containing colloidal dispersion at various intervals. The objective was to generate colloidal dispersion with identical constituents but differing relative particle sizes by subjecting them to ultrasonic vibration for varying durations (0 min, 30 mins, 60 mins, 90 mins, 120 mins). This approach maintained consistency throughout the experimental process, from agitation to measurement, within the confines of the pump circulation system.

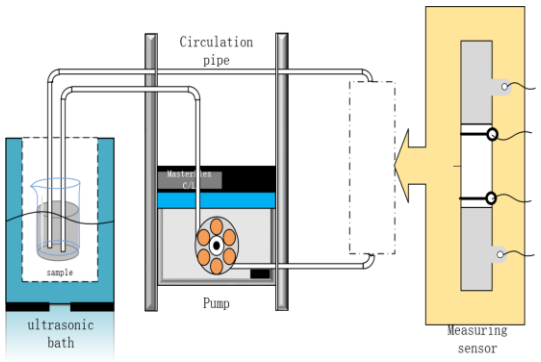

Fig. 1: The structure of the pump circulation system

III. Results

As the silica particles undergo dilution and pretreatment, the physical properties of all treated SiO_2 nanoparticle suspensions, including zeta potential, pH, surface charge and Particle size distribution, are assessed for subsequent analysis. These results are compiled in Table 1 and Table 2.

TABLE I: Concentration, Temperature, differential agitation time,Conductivity and Zeta potential of colloidal dispersion used

Concentration (%wt)	Temperature (℃)	agitation time (mins)	pH	Conductivity (S/cm)	Zeta potential (mV)
0.5%	20.0	0	5.75	2.1	-23.1
0.5%	20.0	30	5.44	3.7	-26.1
0.5%	20.0	60	5.42	4.8	-24.2
0.5%	20.0	90	5.35	7.0	-25.1
0.5%	20.0	120	5.39	8.2	-24.2

TABLE II: Concentration, Temperature, Conductivity and Zeta potential of colloidal suspensions at different concentrations

Concentration (%wt)	Temperature (℃)	agitation time (mins)	pH	Conductivity (S/cm)	Zeta potential (mV)
0.5%	20.0	0	5.75	2.1	-23.1
0.4%	20.0	0	6.7	1.6	-38.1
0.3%	20.0	0	6.34	1.4	-33.8
0.2%	20.0	0	6.54	1.175	-33.6
0.1%	20.0	0	6.36	0.8	-36.8

Table 1 illustrates the changes in temperature, conductivity, pH, and zeta potential for a 0.5%wt colloidal dispersion during ultrasonic vibration. The conductivity generally increases, the pH remains mildly acidic, and the absolute value of the zeta potential is generally below 40 mV, indicating a relatively unstable colloidal state. Typically, this state would require the addition of an alkaline substance to stabilize the dispersion, but to avoid interference with EIS measurements, no stabilizing treatment is applied. When the colloidal dispersion is in an alkaline environment, it leads to an increase in the surface charge within the colloidal dispersion, which further results in an increase in the zeta potential. This makes the particles more inclined to separate due to the elevated zeta potential, thereby causing a stronger potential difference between the particles and the suspension.Table 2 clearly demonstrates that as the particle concentration gradually decreases, the proportion of metal particles within the colloidal dispersion also gradually decreases, which in turn leads to a gradual decline in conductivity. Additionally, since the pH of all colloidal dispersions is below 7, this results in the zeta potential of the colloidal dispersions generally not being high in absolute value.

Prior to agitation, the overall particle size is relatively large. After repeated agitation, the size distribution of particles with a size of approximately 200 nm increases, leading to a reduction in the average particle size within the dispersion. The 0.5%wt

PSD of differential ultrasonication time are Illustrated in Fig 2. At low agitation times, there is a very large aggregate peak which partially reduces as US time increases to form a bimodal distribution. However, even the development of a smaller peak is substantially above the manufacturer estimates for particle size, suggesting the particles continue to be unstable owing to their low surface charge, resulting in aggregated dispersions under all conditions.

Fig 3 presents the size data for different concentrations under low ultrasonication. In this case, the larger concentrations show higher order aggregate peaks, owing to the greater number of particle contacts in higher concentrations

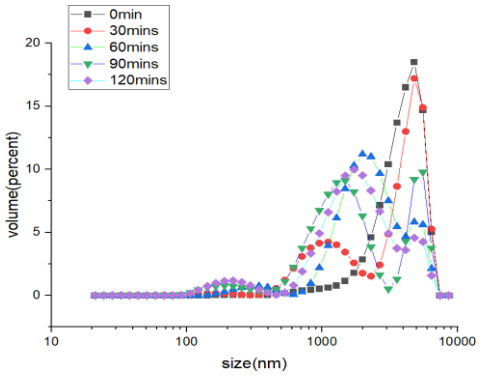

Fig. 2: Particle size distributions of colloidal suspension with different agitation times

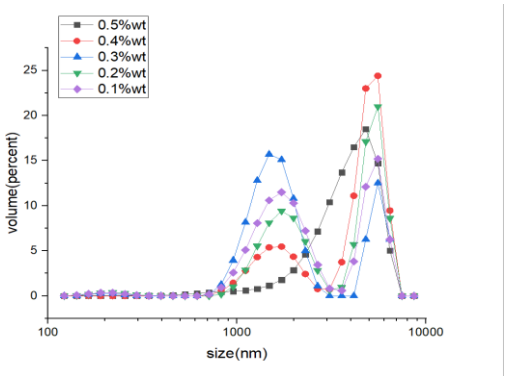

Fig. 3: Particle size distributions of colloidal suspension with different concentration

Figs 4 and 5 depict the impedance phase and magnitude recorded by the Solartron 1260 over the 1 kHz to 1 MHz frequency range for different ultrasonic vibration times. Based on the Figs 4 and 5, as the average particle size decreases, the measured impedance magnitude also decreases, with the relaxation frequency typically around 10 kHz. The absolute value of the impedance phase decreases with the reduction in average particle size at similar frequencies. The primary frequency range for impedance magnitude and phase variations lies between 1 kHz and 100 kHz, with impedance magnitude under 1 MΩ.

It can also be seen by comparing Figs 3 and 6, that when colloid dispersions of different concentration are used, a similar trend is observed that is inversely proportional to particle concentration. So, in this case, lower concentration dispersions showing lower levels of aggregation also lead to greater phase shifts and greater peak magnitudes. Correspondingly, greater concentrations that are more aggregated lead to lower phase shifts and magnitudes.

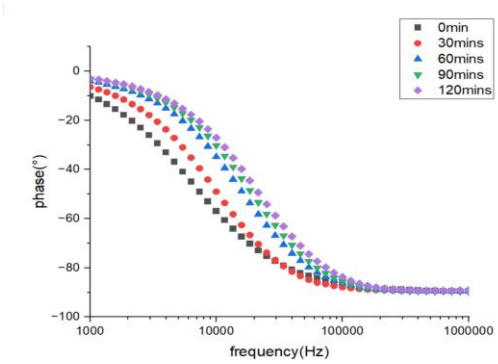

Fig. 4: The 0.5%wt nanoparticle dispersion phase shift measured by EIS within different ultrasonic vibration times

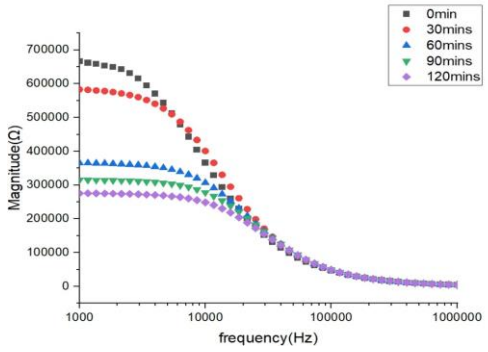

Fig. 5: The 0.5%wt nanoparticle dispersion magnitude ratio measured by EIS within different ultrasonic vibration times

Additionally, according to Fig 2, Fig 4, when nanoparticles have a diameter smaller than 1000 nm, relative changes in the average particle size are reflected in relative changes in the impedance phase and magnitude. For instance, the impedance magnitude and phase values for a colloidal dispersion with an average particle size of 950 nm are significantly higher than those for colloidal dispersion with other particle sizes. When the relative change in average particle size is around 100 nm, the relative changes in impedance magnitude and phase remain relatively consistent across 60 minutes, 90 minutes, and 120 minutes.

The impedance magnitude and phase obtained through EIS can be used to simplify a parallel RC equivalent circuit model. The relationships between the impedance phase and magnitude with the RC parameters in the parallel circuit are as follows:

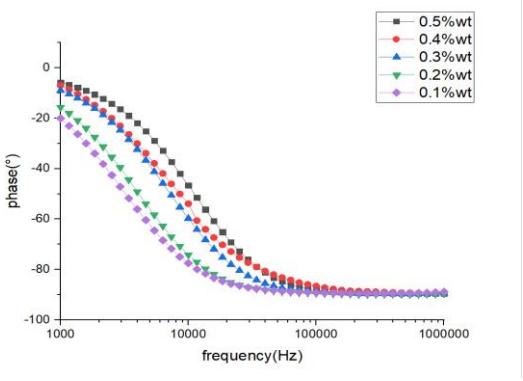

Fig. 6: Phase shift of nanoparticle dispersions at different concentrations measured by EIS with the same ultrasonic vibration times.

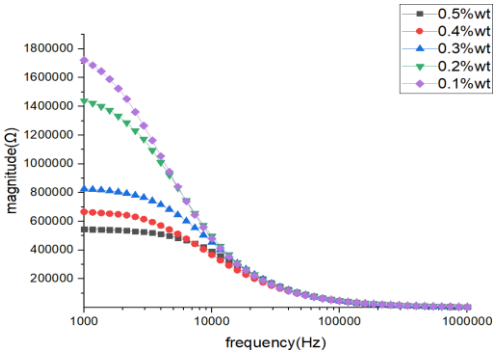

Fig. 7: Different concentration nanoparticle dispersion magnitude ratio measured by EIS within the same ultrasonic vibration times.

$$\theta = \arctan(-\omega RC) \tag{1}$$

$$|Z| = \frac{1}{\sqrt{\omega^2 C^2 + \frac{1}{R^2}}} \tag{2}$$

The phase angle formula for an RC parallel equivalent circuit model can also be represented as:

$$\tan(\theta) = -\omega RC = -\frac{\omega C}{G} \tag{3}$$

where G is conductance, and ω is the angular frequency. The relationship between capacitance and conductance can be expressed as:

$$C = \frac{A}{d}\varepsilon_0\varepsilon_r = \varepsilon_0(1+\chi_e)k \tag{4}$$

$$G = k\sigma \tag{5}$$

Here, ε_0 is the permittivity of free space, ε_r is the relative permittivity, A is the cross-sectional area of the RC resistor, and d is the length of the RC resistor. k is the cell constant, k is the conductivity of the colloidal dispersion, and χ_e is the electric susceptibility. Substituting into the above formula, the following expression is derived [3]:

$$\tan(\theta) = -\frac{\omega C}{G} = \frac{\kappa\omega\varepsilon_0(1+\chi_e)}{\sigma} = \frac{k\omega\varepsilon_0\chi_e}{\sigma} \tag{6}$$

The relationship between ε 0 χ e and the particle diameter can be derived from the work of Dukhin [4] and Jimenez [5]:

$$\varepsilon_0\chi_e = \frac{3\phi\varepsilon_0}{4\pi}\frac{2K_S - K_a}{2(K_S K_a)} \tag{7}$$

where is ϕ the particle volume fraction, K_S is the surface conductivity, and K_a is the conductivity of the solvent.

$$\tan(\theta) = \frac{\kappa\omega\varepsilon_0}{\sigma} - \frac{k\omega\varepsilon_0\chi_e}{\sigma} = \frac{\kappa\omega\varepsilon_0}{\sigma} - \frac{k\omega\varepsilon_0}{\sigma}\frac{3\phi\varepsilon_0}{4\pi}\frac{2K_S - K_a}{2(K_S K_a)}$$

IV. CONCLUSION

In this study, an ultrasonic bath is used to agitate the particles in a nano-colloidal dispersion causing relative changes in particle size, EIS shows high sensitivity to changes in the phase and magnitude of the impedance in the equivalent model due to the polarization of nanoparticles caused by these size changes. As a result, EIS measurement of the changes in particle size in colloidal dispersions is feasible and may become a novel method for measuring the size distribution of nanoparticles.

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