

Separation and Manipulation of Rare-earth Oxide Particles by Dielectrophoresis^{*}

CHEN Huiying (陈慧英)^{1,**}, LIU Yan (刘艳)², ZHANG Heteng (张鹤腾)², YU Le (于乐)², ZHU Yuelin (朱岳麟)¹ and LI Di (李荻)¹

¹ School of Material Science and Engineering, Beihang University, Beijing 100083, China

² College of Life and Environmental Science, Minzu University of China, Beijing 100081, China

Abstract A challenge in chemical engineering is the separation and purification of rare-earth elements and their compounds. We report the design and manufacture of a dielectrophoresis (DEP) microchip of microelectrode arrays. This microchip device is constructed in order to use DEP to capture micro-particles of rare-earth oxides in petroleum. Dielectrophoretic behavior of micro-particles of rare-earth oxides in oil media is explored. The dielectrophoretic effects of particles under different conditions are investigated. It is showed that the prepared microchip is suitable for use in the investigation of dielectrophoretic responses of the rare-earth oxides in oil media. The factors such as frequency, particle size and valence of rare-earth metal are discussed. When the frequency is fixed, the translation voltage decreases as particle size increases. Lower frequencies are more effective for manipulation of inorganic particles in oil media. Particles of the same rare-earth oxide with different size, as well as particles of different rare-earth oxides, are captured in different regions of the field by regulating DEP conditions. This may be a new method for separation and purification of particles of different rare-earth oxides, as well as classification of particles with different size.

Keywords dielectrophoresis, microchip, rare-earth oxide, separation

1 INTRODUCTION

Dielectrophoresis (DEP) involves induced polarization and motion of particles suspended in a medium with different dielectric characteristics when an AC electrical field is applied. It has the advantage of operating at lower voltages, so in recent years it has become one of the most widely used techniques for separating particles by microfluidic manipulation and received increasing attention in microfluidics [1]. Since its discovery by H. A. Pohl in 1956, DEP has undergone significant development and is now used widely in biology, chemistry, medicine, environmental science and nano-technology [2].

Pohl gave the definition of dielectrophoresis [3] after his pioneering research on inorganic particles using DEP from the late 1950s to the mid 1960s. During the past decades, the application of dielectrophoresis to collecting, positioning and separating particles suspended in liquids has advanced tremendously due to improvements in the micro-fabrication techniques [4], which is useful for routing particles to precise locations in microfluidic channels [5]. DEP forces are variable and can be modified simply by changing frequencies or by arranging different sets of electrodes in an array to modify the shape of the DEP focusing [5]. DEP has been widely applied to purification [6] and assembly [7] of carbon nanotubes to prepare nano-devices [8], and to concentration from mineral wastes [9] and purification of petroleum products [10]. With recent rapid development of lab-on-a-chip technologies, DEP has been extensively applied to on-chip

manipulation of artificial or biological particles [11].

Metal oxide micro-particles, especially nano-particles [12], may be useful in cosmetics, paints and environmental treatment due to their outstanding performance in whitening and photocatalysis. Rare-earth elements and their compounds, due to their special structure of 4f electrons, have a wide range of applications in optical materials, magnetic materials, catalysts and medicines. Products of rare-earth oxides with high purity have extensive uses in industries and technologies because of their special physical and chemical properties [13]. However, the separation of these compounds is very difficult since the properties of different rare-earth elements are quite similar. At present, the separation and purification of rare-earth is mainly carried out by wet methods such as ion-exchange and solvent extraction, which often require multiple repetitions to achieve adequate purity. Therefore, it remains an important goal in rare-earth chemistry to find efficient and widely applicable methods [14]. A major challenge in the chemical industry is to innovate new processes with less pollution and high energy efficiency [15]. Of various available techniques, DEP is useful in separation of some micro- or nano-particles, which are difficult to classify by traditional physical or biochemical methods [5–7].

In this study, we prepare a μm -scale DEP micro-array chip, assemble an experimental system and investigate the DEP response to several rare-earth oxides. Different conditions are applied for the capture of different rare-earth oxide particles and classification of particles with different size. Separation by DEP

Received 2010-03-19, accepted 2010-08-11.

^{*} Supported by the 985 Foundation of Central University for Nationalities (CUN985-3-3) and the National Natural Science Foundation of China (90305011).

^{**} To whom correspondence should be addressed. E-mail: huiyingrchen@yahoo.com.cn

does not require additional reagents or processing, so it is an environmentally friendly technique.

2 THEORY

Subjected to a non-uniform electric field E_0 , a neutral but polarizable particle of radius R and density ρ_p suspended in a medium of permittivity ϵ_m experiences a time-averaged DEP force F_{DEP} ,

$$F_{\text{DEP}} = 2\pi R^3 \epsilon_m \text{Re}[K(\omega)] \nabla E^2 \quad (1)$$

where ω is the field frequency and $K(\omega)$ is the Clausius-Mossotti factor, which describes the electrical properties of the particle and the medium [16], $\text{Re}[K(\omega)]$ stands for the real part of $K(\omega)$.

$$K(\omega) = \frac{\epsilon_p^* - \epsilon_m^*}{\epsilon_p^* + 2\epsilon_m^*} \quad (2)$$

$$\epsilon^* = \epsilon - i \frac{\sigma}{\omega} \quad (3)$$

E is the root mean square (rms) value of the electric field, ϵ^* the complex permittivity, subscripts p and m denote particle and medium, respectively.

If $\text{Re}[K(\omega)] > 0$, i.e. the electrical polarizability of particles exceeds that of the suspending medium, the particles tend to move to the regions with strong electric field, positive DEP. In the case of negative DEP, the particles will move towards weak-field regions. The direction of DEP depends on the polarizability as well as the applied frequency [17]. Particles can be trapped in or released from a specific area by applying electrical signals with suitable frequency and amplitude [16].

3 EXPERIMENTAL

We chose one particle for investigation, located between the tips of a pair of opposite electrodes. The particle diameter was measured using analytic software (DN-2, YXOPT, China). Fig. 1 shows the principle of positive dielectrophoresis.

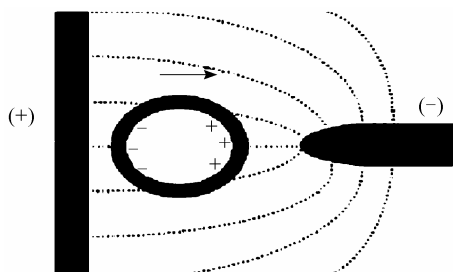


Figure 1 The principle of positive dielectrophoresis [3]

3.1 Experimental apparatus

The electrode arrays of the microchip comprise several inter-parallel fingers (100 μm long, 20 μm

wide, and 20 μm inter-electrode gap). We designed the pattern and the size of the chip. The microelectrodes were fixed on an insulating substrate by a vacuum evaporation technique (ISCAS) (Fig. 2). The electrodes were deposited on quartz glass substrates. The polymethyl acrylate chamber (40 mm×10 mm×1 mm) was conglutinated with UV curing adhesives. The electrode array was connected to a signal generator and was observed using a digital video camera attached to a PC (Fig. 3).

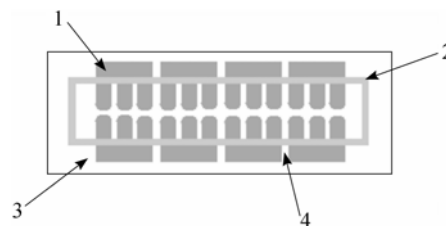


Figure 2 A schematic drawing of the chamber
1—microelectrode arrays; 2—chamber wall of polymethyl acrylate; 3—glass substrate; 4—gap between arrays

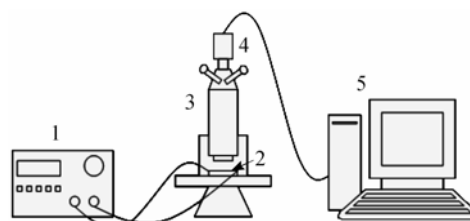


Figure 3 Schematic for DEP
1—signal generator; 2—DEP microchip; 3—microscope; 4—video; 5—PC

3.2 Particles, media and experimental procedure

The particles of rare-earth oxides were suspended in aviation kerosene (1.0 g·L⁻¹ final concentration). Its conductivity was measured with a conductivity meter (DDS-11D, Shanghai Lida, China). An ultrasonic dispersion device was used to avoid particle aggregation. The liquid sample (~15 μL) was injected into the chamber. Then the DEP trapping of particles to the microelectrode was performed with AC voltage in frequency of 20–200 kHz and amplitude of 5–100 V.

3.3 Field generation and observation

AC fields were applied using a signal generator (SG1648 Hongze, Jiangsu, China). The frequencies of the generator were in the range from 10 Hz to 2 MHz with amplitudes of 0–150 Vp-p. Positive DEP of the particles occurred when AC electricity was applied to the electrodes. Observations were made using a microscope (CN-15, KONKYO, YXOPT, China) and a video camera (HDCE-30, YXOPT, China), connected to a computer and video recorder for data collection and analysis. Particle diameters were determined using analysis software (DN-2, YXOPT, China). All

experiments were performed in a static state.

4 RESULTS AND DISCUSSION

4.1 Relationship between voltage and radii of particles

Figure 4 shows that the translation voltages (TV) of particles decrease with increasing radii of rare-earth oxide particles under positive DEP. The bigger particles are captured more easily. This can be explained using Eq. (1). F_{DEP} is proportional to R^3 , the radius of particle. When particles with similar sizes, such as 2.3–3.0 μm in this case, are put in different regions of a non-uniform electric field under the same voltage, the particles of the same oxide can be classified according to their sizes. Yasukawa *et al.* [18] also separated micro-particles of different sizes based on DEP in a channel [18]. When the difference in particle size is very small, multi-step DEP can be used to achieve the separation [19].

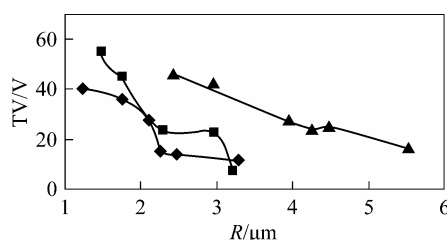


Figure 4 Relationship between TV and radius of rare-earth oxide particles

■ Dy₂O₃; ▲ CeO₂; ◆ La₂O₃

4.2 Effect of frequency on translation voltage

Particles of similar size were selected to investigate the effect of variation in frequency. Fig. 5 shows that the particles translate more readily at lower frequencies under positive DEP. A lower frequency is better to manipulate particles of rare-earth oxides using DEP. This is consistent with the previous result [20], in which the positive DEP in a latex-in-water system is in an extremely low frequency range, around 15 Hz. However, biological particles exhibit positive

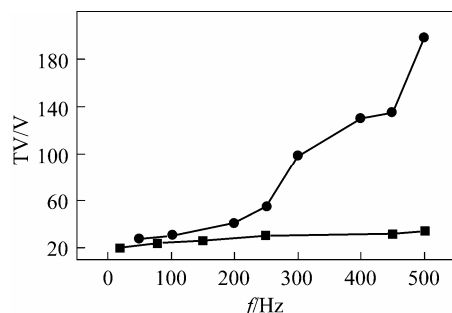


Figure 5 Relationship between TV and frequency

■ Dy₂O₃; ▲ CeO₂

DEP in a high frequency range. Under our experimental conditions, we lowered the frequency to make the particles exhibit positive DEP at low voltage. Al-daeus *et al.* [19] observed that a lower frequency could increase the positive dielectrophoretic motion due to the formation of counter-ion cloud. It can be also seen from Eqs. (1) and (3) that as frequency ω increases, the dielectric constant ϵ of particle decreases. The particle with lower dielectric constant requires higher field strength.

Figure 5 shows that as the frequency increases, the translation voltage of dysprosium oxide changes little, while the translation voltage of cerium oxide increases greatly. In the same medium we can separate different rare-earth oxides completely in the dielectrophoretic separation device, by adjusting the voltage at a given frequency (500 Hz). Chen *et al.* [21] pointed out in their study on dielectrophoretic behavior of polystyrene particles that different particles can be separated on the basis of the parameters, in particular the frequency of electric field, dielectric properties of particles and the surrounding medium. And Wei *et al.* [22] found, in their research of CNT sorting, frequency is more important than the number of purification. This will be significant for practical implementation of DEP to separate different particles for biosensors and medical application [23].

4.3 Effect of valence of the metal in rare-earth oxides

For the sizes within 2.392–2.972 μm and the frequency at 50 Hz, the relationship between the translation voltage of rare-earth oxide particles and valences of the rare-earth metals are investigated. Table 1 shows that the translation voltages of different rare-earth oxide particles differ although the particle sizes are close. Particle with higher valence requires higher voltage for DEP translation. This result is significant, which implies that particles with different valences may be captured at a fixed frequency by adjusting the voltage. If the difference in valences for two rare-earth oxides is small, as for La₂O₃ and Dy₂O₃ in Table 1, we can still separate different rare earth oxides by means of multi-step DEP. For metals with significantly different valences, their oxides, such as La₂O₃ and CeO₂, or Dy₂O₃ and CeO₂, can be easily separated using DEP.

Table 1 The translation voltage of rare-earth oxide particles of different valences

Particle name	Particle radius/ μm	Translation frequency/Hz	Translation voltage/V	Metal valence
dysprosium oxide	2.792	50	14	3
lanthanum oxide	2.972	50	22.5	3
cerium dioxide	2.914	50	40	4

In summary, DEP behavior of three types of rare-earth oxide particles in an oil medium was explored

by using a micro-fabricated electrode system. Within a certain range of particle size, particle translation voltage decreases as particle size increases. Particles of the same rare-earth oxide can be classified based on their sizes by regulating the voltage. Low frequencies are better to manipulate rare-earth oxide particles by DEP, so that it is energy-efficient. Rare-earth oxides with different valences can be separated. Under higher frequency conditions, rare-earth oxide particles with different size are captured using one-step DEP by regulating the voltage. At frequency of 50 Hz different rare-earth oxides may be separated by means of multi-step DEP.

ACKNOWLEDGEMENTS

We are grateful to Dr. Andrew Perrett for English revision.

REFERENCES

- 1 Cao, J., Cheng, P., Hong, F., "A numerical analysis of forces imposed on particles in conventional dielectrophoresis in microchannels with interdigitated electrodes", *Journal of Electrostatics*, **66**, 620–626 (2008).
- 2 Zhang, H., Han, P., Shen, G., Dai, J., Chen, H., "Dielectrophoresis and its application for separation of inorganic", *Journal of the Central University for Nationalities (Natural Sciences Edition)*, **17**, 45–51 (2008).
- 3 Pohl, H.A., *Dielectrophoresis*, Cambridge University Press, Cambridge (1978).
- 4 Kadaksham, J., Singh, P., Aubry, N., "Manipulation of particles using dielectrophoresis", *Mechanics Research Communications*, **33**, 108–122 (2006).
- 5 Ravula, S.K., Branch, D.W., James, C.D., Townsend, R.J., Hill, M., Kaduchak, G., Ward, M., Brenner, I., "A microfluidic system combining acoustic and dielectrophoretic particle preconcentration and focusing", *Sensors and Actuators B: Chemical*, **130**, 645–652 (2008).
- 6 Liu, X., Spencer, J.L., Kaiser, A.B., Arnold, W.M., "Selective purification of multiwalled carbon nanotubes by dielectrophoresis within a large array", *Current Applied Physics*, (6), 427–431 (2006).
- 7 Seo, Y., Kumar, S., Kim, G., "Photoconductivity characteristics of ZnO nanoparticles assembled in nanogap electrodes for portable photodetector applications", *Physica E*, **42**, 1163–1166 (2010).
- 8 Suehiro, J., Imakiire, H., Hidaka, S., Ding, W., Zhou, G., Imasaka, K., Hara, M., "Schottky-type response of carbon nanotube NO₂ gas sensor fabricated onto aluminum electrodes by dielectrophoresis", *Sensors and Actuators B: Chemical*, **114**, 943–94 (2006).
- 9 Lungu, M., "Separation of small metallic nonferrous particles in low concentration from mineral wastes using dielectrophoresis", *Mineral Processing*, **78**, 215–219 (2006).
- 10 Chen, H., Huang, H., Zhu, Y., Li, D., "The effects of refining efficiency of the diesel fuel by dielectrophoresis", *Petroleum Processing and Petrochemicals*, **40**, 51–54 (2009). (in Chinese)
- 11 Kang, Y., Cetin, B., Wu, Z., "Continuous particle separation with localized AC-dielectrophoresis using embedded electrodes and an insulating hurdle", *Electrochimica Acta*, **54**, 1715–1720 (2009).
- 12 Liu, Z.P., Pei, L.X., Ji, H.B., Yao, X.D., "Preparation of well-shaped microcapsule immobilizing inorganic nanoparticles", *Chin. J. Chem. Eng.*, **16** (3), 384–388 (2008).
- 13 Lin, H., "Production practice of high-purity rare-earth oxides", *Sichuan Nonferrous Metals*, (2), 2–6 (2008). (in Chinese)
- 14 He, P., Cang, D., Zong, Y., "Separation of rare earth elements from their binary oxide mixtures via chemical vapor transport reaction", *Chinese Rare Earths*, **26**, 53–56 (2005).
- 15 Chen, G.W., Yue, J., Yuan, Q., "Gas-liquid microreaction technology: recent developments and future challenges", *Chin. J. Chem. Eng.*, **16** (5), 663–669 (2008).
- 16 Paul, R., Kaler, K.V.I.S., "Theory of electrode polarization in dielectrophoresis and electrorotation", *Journal of Colloid and Interface Science*, **194**, 225–238 (1997).
- 17 Crews, N., Darabi, J., Voglewede, P., Guo, F., Bayoumi, A., "An analysis of interdigitated electrode geometry for dielectrophoretic particle transport in micro-fluidics", *Sensors and Actuators B: Chemical*, **125**, 672–679 (2007).
- 18 Yasukawa, T., Suzuki, M., Shiku, H., Matsue, T., "Control of the microparticle position in the channel based on dielectrophoresis", *Sensors and Actuators B: Chemical*, **142**, 400–403 (2009).
- 19 Aldaeus, F., Lin, Y., Amberg, G., Roeraade, J., "Multi-step dielectrophoresis for separation of particles", *Journal of Chromatography A*, **1131**, 261–266 (2006).
- 20 Molla, S.H., Bhattacharjee, S., "Prevention of colloidal membrane fouling employing dielectrophoretic forces on a parallel electrode array", *J. Membr. Sci.*, **255**, 187–199 (2005).
- 21 Chen, D.F., Du, H., Li, W.H., "Bioparticle separation and manipulation using dielectrophoresis", *Sensors and Actuators A*, **133**, 329–334 (2007).
- 22 Wei, C., Wei, T.Y., Tai, F.C., "The characteristics of multi-walled carbon nanotubes by a two-step separation scheme via dielectrophoresis", *Diamond and Related Materials*, **19**, 573–577 (2010).
- 23 Jiang, K., Liu, W., Wan, L., Zhang, J., "Manipulation of ZnO nanostructures using dielectrophoretic effect", *Sensors and Actuators B: Chemical*, **134**, 79–88 (2008).