

Electrokinetic Characterization of Nanoscale Metal Oxide Films

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Abstract:

In this work, we constructed a device to characterize the zeta potential of metal oxide films using electrokinetic forcing. In preparation, we characterized aluminum oxide tracer particles in a Malvern Zetasizer over a range of pH and salt concentrations. Then, we prepared oxide films of controlled thickness and chemistry, which were used to define a parallel-plate electrokinetic cell. With the particles suspended in fluids of varying salt concentrations and pH, we applied a voltage to generate an electroosmotic flow in the channel. Through measurements of the particle motion with particle image velocimetry (PIV) we could determine the zeta potential of the solid surface.

Introduction:

In micro- and nano-scale systems, electrokinetics plays an important role in determining the physical and chemical attributes of a system. Many solid surfaces become charged in the presence of a liquid due to (a) ionization of surface groups, and (b) adsorption of ions in solution onto a surface [1]. The charge of a surface will change as the salt concentration and pH of a solution are varied. The electrical potential, or zeta potential, is a measure of the electrokinetic properties of the surface.

Determination of the zeta potential of a surface in solutions of defined pH and salt concentration enables better understanding of the interactions between particles and surfaces. Knowledge of surface zeta potential is relevant to a wide variety of applications which involve a chemical interaction between particles and solutions.

$$\mathbf{u} = \frac{-\epsilon_0 \epsilon}{\eta} (\zeta_p + \zeta_w) \nabla \phi$$

\mathbf{u} : particle velocity

ζ_p : particle zeta potential

ζ_w : wall zeta potential

ϕ : external electric field

η : viscosity of solution

ϵ : electrical permittivity of solution

Figure 1: By measuring the velocity of particles under an electric field, we could characterize the zeta potential of the surface if the zeta potential of the particles was known.

In this work, we combined electroosmotic forcing and particle electrophoresis to determine the zeta potential of metal oxide surfaces in a custom built electrokinetic device. Using PIV, we could determine the velocity of a particle undergoing electrophoresis in an electroosmotic flow. The particle velocity can be used to determine the zeta potential of the wall, if the particle zeta potential is known, as shown in the equation in Figure 1 [2].

Particle Preparation and Characterization:

We first prepared solutions over a range of salt concentrations and pH; using sodium chloride (NaCl), we prepared 0.1 mM, 1 mM, and 10 mM solutions between pH 1 and 5, using HCl. We then cleaned the 700 nanometer alumina particles by mixing 0.03 grams of alumina particles in a 50 mL solution of deionized water, sonicating the particles to ensure proper dissolution, and centrifuging the particles for 20 minutes at 2500xg. The alumina particles would sediment to the bottom of the flask, and we exchanged the fluid in the flask for another 50 mL of deionized water. The process was repeated a total of three times, after which the particles were removed and dried in an oven for two hours. The particles were then mixed with solutions of known pH and salt concentration, and sonicated.

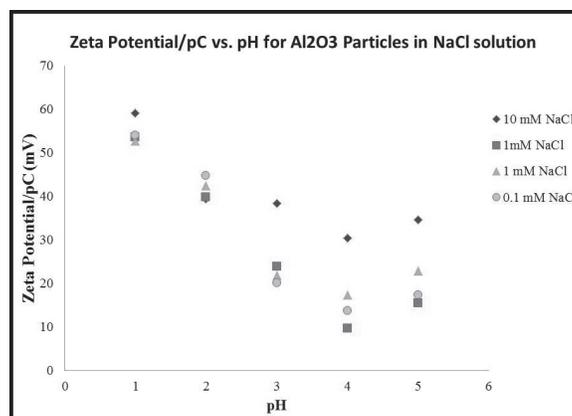


Figure 2: The zeta potential normalized by the counter ion concentration of the alumina particles showed a strong dependence on pH, but minimal variation with respect to salt concentration.

To characterize the zeta potential of the alumina particles, we used a Malvern Zetasizer Nano, which measures properties of suspended particles using dynamic light scattering. We characterized the particle zeta potential in the various solutions described above, as shown in Figure 2. Measured alumina particle zeta potentials were consistent with literature values [3].

Device Fabrication and Experimental Setup:

To fabricate the device, we deposited 300 nm of hafnium oxide (the material of interest) onto two 25 mm × 75 mm glass slides. One glass slide had two thru holes located 40 mm apart along the slide centerline. The two Hafnia substrates were assembled to sandwich a 127 μm Teflon® shim with a center removed, forming a 127 μm tall channel between the Hafnia surfaces. We sealed the edges with epoxy to prevent leaks. We fabricated large reservoirs above the thru holes to minimize surface tension effects and pressure gradients. A cross-section of the device is presented in Figure 3.

To run an experiment, we used a function generator, an amplifier, a voltmeter, two platinum electrodes, a camera, and a Nikon Eclipse TE2000-u inverted microscope. Initially, we filled the channel of our fabricated device with alumina particles suspended in solution. We then generated a square wave, amplifying the signal to our desired voltage, and used this field to actuate fluid in the device via platinum electrodes inserted in the reservoirs. The alumina particles suspended in salt solution could be tracked by taking a sequence of images using a camera, and the particle velocity could be measured via PIV. The experimental setup is shown in Figure 4.

Conclusions and Future Work:

In this work, we were able to successfully construct an electrokinetic device that can be used to determine the zeta potential of metal oxide films deposited on glass substrates. Our future work will be to calculate the zeta potential of hafnium oxide over a new range of pH using particle image velocimetry, fabricate similar devices for other metal oxide films, and improve the overall design of our device.

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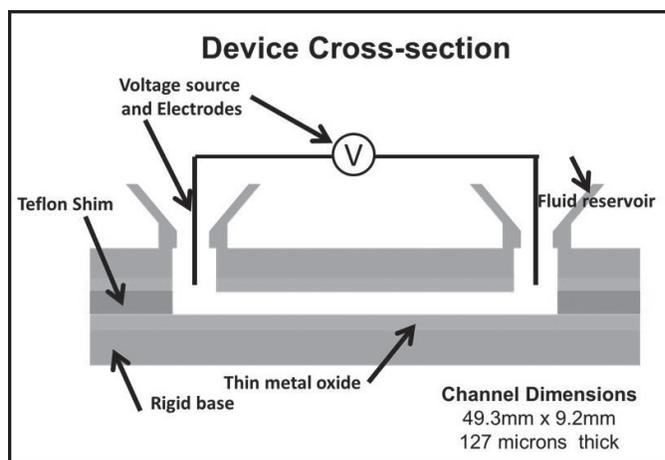


Figure 3: The relatively small channel thickness allowed us to assume 2D motion of alumina particles across the channel.

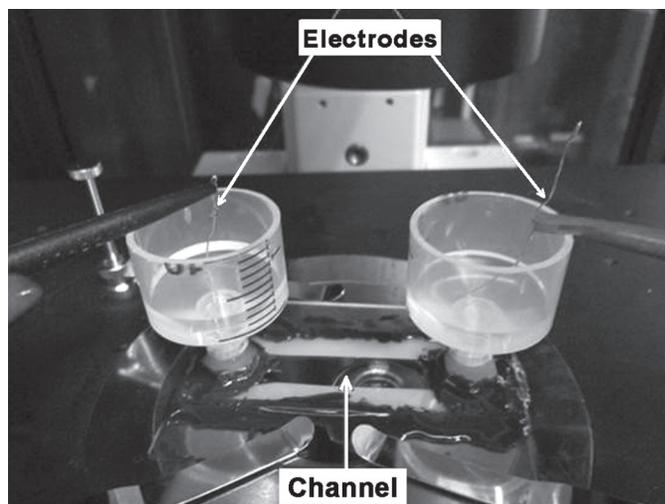


Figure 4: Using an inverted microscope and camera, we tracked alumina particles as they moved through the channel under an electric field.

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