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Characterizing zeta potential of functional nanofibers in a microfluidic device

Daehwan Cho [a], SangGap Lee [b,c], Margaret W. Frey [a,*]

[a] Department of Fiber Science and Apparel Design, Cornell University, Ithaca, NY 14850, USA
[b] Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14850, USA
[c] Division of Materials Science, Korea Basic Science Institute, Daejeon 305-333, South Korea

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ABSTRACT

The measurement of surface charge on nanofibers was achieved by characterizing zeta potential of the nanofibers via a newly developed device for streaming current measurement. Low flow rates were sufficient to generate detectable streaming currents in the absence of an externally applied voltage without damaging nanofiber samples. Zeta potential was calculated by using the Helmholtz–Smoluchowski equation and the measured streaming currents. Two acrylic plates were machined and assembled to form a microfluidic channel that is 150 μm high, 2.0 mm wide, and 30 mm long. Two electrodes for the measurement of streaming currents were housed in the top plate. Two nanofibers of pure polyacrylonitrile (PAN) fibers and charged (TiO_2 incorporated) PAN fibers were prepared and characterized in the device. Monobasic sodium phosphate and dibasic sodium phosphate were used to prepare four different pH buffer solutions ranging from pH 5 to pH 8 in order to characterize the zeta potentials. The pure PAN nanofibers had negatively-charged surfaces regardless of pH. However, the zeta potentials of PAN/TiO_2 nanofibers changed from positive to negative at pH 6.5. The zeta potential measurements made on the nanofibers in this new microfluidic device matched with those of the powdered raw materials using a commercial Zetasizer.

1. Introduction

The surface charges on materials are closely related to affinity-associated interactions. Therefore, surface-charged materials have been critical in performance of filtration membranes [1–3], electrokinetic particle transport systems [4,5], and bioanalysis sensors [6,7]. Surface charges can control the degree of biomolecular affinity on a material surface. In biomolecular detection, surface-charged nanofibers concentrate target biomolecules via electostatic attraction between the nanofibers and the countercharges of target molecules, enabling improved detection sensitivity. In the area of air filtration, electrostatically charged fibers attract and capture countercharged particles or dust that passes through the filter media. With high specific surface area and a broad range of chemistry available, nanofiber mats with charged surfaces are ideal candidates for sensor and filter applications [8–10].

A wide variety of surface-charged functional materials have been manufactured, and many studies have been devoted to developing methods for estimating their surface charges [11–15]. Berger et al. outlined the most prominent electrical modes for investigation of properties of conductive surfaces in scanning probe microscopy [15], which has been used extensively to measure localized electric properties of materials. The force gradients measured between a biased conductive conical tip and a hemispherical dielectric sample were shown to be model-able, providing the surface charge density and the dielectric constant of the sample [16]. Ignatova et al. and Cho et al. measured the thermally stimulated current (TSC) spectra to evaluate the charge storage performance of electrospun fiber mats [17,18]. While TSC can provide some confirmation of surface charge on electrospun fibers, the measurements are dependent on sample size and do not indicate the intrinsic surface potential of the fibers. Zeta potential measurements are capable of determining the intrinsic surface potential of materials.

Zeta potential (surface electric potential; denoted as a Greek letter ζ) was introduced as a parameter describing the electric potential in the solid/liquid interfacial layer of a material in an aqueous solution, being an important and useful indicator of surface charges [19,20], which is required to predict and control the stability of colloidal suspensions or emulsions. Zeta potential in colloidal systems is a controlling parameter in processes such as adhesion, surface coating, filtration, lubrication, and corrosion [4,21,22]. As illustrated in Fig. 1, positive and negative ions are distributed in the solid/liquid interfacial layer. When a material is immersed in an electrolyte solution, the functional groups on the material surface are protonated or ionized and the counterions of the surface charges gather onto the surface. An electrical double

* Corresponding author. Fax: +1 607 255 1093.
E-mail address: mfw24@cornell.edu (M.W. Frey).

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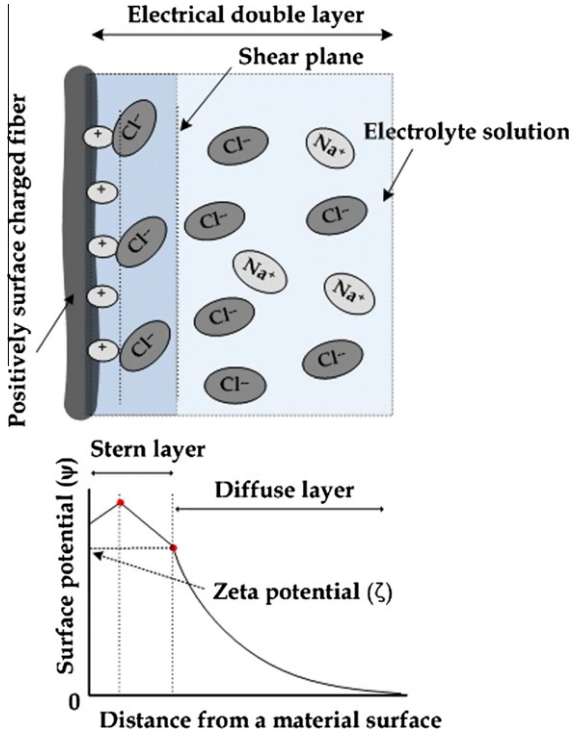

Fig. 1. Schematic diagram of charge distribution in a solid/liquid interfacial layer of buffer solution according to the Gouy–Chapman–Stern–Grahame model.

layer (well defined by Gouy–Chapman–Stern–Grahame model [19,20,23–25]) is formed at the interfacial boundary by attractive forces between a surface-charged material and counterions. The counterions strongly attached to surface charges are hardly separated from the surface by external forces. This layer is called as Stern layer. Outside the Stern layer is a Gouy–Chapman diffuse layer in which the counterions are of lower concentration and not firmly bound to the material surface. The counterions in the diffuse layer are easily mobile by thermal diffusion. The electric potential $\psi(x)$ at the distance x from the surface decreases linearly with the increase of x in the Stern layer and then decays exponentially to zero in the diffuse layer. The electric potential in the electric double layer is neutralized over the diffuse layer where the bulk solution is encountered. As counterions are firmly bound to the surface charges within Stern layer and sheared off in the diffuse layer, a boundary (shear plane) is formed between the two layers. Zeta potential is defined as the electric potential at the location of the shear plane.

Electrokinetic effects result from the relative motion of ions between the Stern layer and the Gouy–Chapman diffuse layer formed around a surface-charged material in an electrolyte solution. Electrokinetic potentials are closely related to the driving force (pressure drop making solution flow), the surface property of the material, and the solution properties (ionic strength, pH). Electrokinetic potentials are largely classified into three categories: electrophoresis, electroosmosis, and streaming potential (or currents).

In Table 1, we summarized the zeta potential measurement methods and their features. In the case of electrophoretic light scattering measurement, the charged particles suspended in the electrolyte are attracted toward the electrode of opposite charge when an electric field is applied across an electrolyte. At that moment, the mobility of charged sample particles is measured to calculate the zeta potential. The large aspect ratio of nanofibers influences mobility in the electrolyte such that zeta potential cannot be measured by this method. In electroosmosis measurement, the zeta potential can be calculated by measuring the motion of liquid induced by an applied potential across a porous and rigid stationary charged media. For nanofibers, the streaming potential is the most appropriate method to measure the zeta potential in a stationary solid phase and a mobile liquid phase. In the streaming potential and streaming current methods, an electric field is generated when a liquid is forced to flow through a stationary charged surface. The instruments under general use based on conventional streaming method, such as SurPASS (SurPASS Electrokinetic Analyzer, Anton Paar GmbH, Austria), require high flow rates to generate detectable streaming potentials and may destroy the morphology of low modulus nanofiber. The microfluidic channel device described here employs low flow rates and a rectangular micro-shaped channel which generate the streaming current through the small size of microfluidic channel.

The zeta potential of solid materials has been investigated by measuring the charges formed at the interface between a solid material and an electrolyte since the early 1900s. Ball and Fuerstenau presented a review of the streaming potential measurements reported from early 1900s through 1970s [26]. In this literature review, the relationship between streaming potential and pressure difference was clearly described, and a method for determining the ratio of the streaming potential to the pressure difference was established. Electrokinetic measurements of various materials including bulk cotton, large bundles of silk, and minerals were characterized to determine their zeta potential. Möckel et al. carried out the computational fluid dynamic calculations to confirm that a self-made tangential flow cell could meet the hydrodynamic stipulations of laminar, steady, and established electrolyte flow for reproducible electrokinetic measurements [27]. Renaud et al. presented a simple method to determine the zeta potential of a microfluidic substrate material shaped into circular and square cross-sectional capillaries by measuring streaming current [28]. Kirby summarized the theory and experimental techniques of zeta potential and reviewed the zeta potential measurements for a variety of polymeric microfluidic substrate materials [12,13]. These previously reported methods of zeta potential measurement, summarized above, have focused on the characterization of rigid films, channel substrates, and bulk materials and have limited capability to measure a low-strength material such as polymeric nanofibers. Matsumoto et al. used a commercialized instrument (SurPASS) equipped with a specially designed clamping cell to measure zeta potential of chitosan nanofiber fabric [29]. However, some studies showed that the instrument under general use requires high flow rates (50–120 mL/min) and bulky samples to generate detectable streaming potentials [30]. Overall, it remains difficult to in situ evaluate the charge potential of surface-charged nanofibers placed in microfluidic devices, particularly in slow flow rates (5–20 μL/min). As briefly described above, the reported methods and the existing instruments for the measurement of zeta potential have so far stayed incapable of measuring the surface charge of a small amount of low modulus nanofibers. In fact, streaming current measurements are fairly commonplace for large porous materials [31,32] and have an advantage that, unlike in streaming potential measurements, surface conduction effects are negligible [24].

To overcome the limitations of previous techniques, pressure-driven flow through a rectangular-shaped channel device was adopted to generate electrokinetic effects across nanofibers. Here we present the development of a new microfluidic technique for the measurement of zeta potential at the surfaces of nanofibers. The streaming currents induced by pressure-driven flows were measured in the absence of an externally applied voltage using an electrometer and used to calculate zeta potential of a material. The geometry of the rectangular channel designed in the present