Low-cost spin-coatable, transferable, and high-κ ion gel dielectric for flexible electrowetting

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ABSTRACT

A novel ion gel material was demonstrated as a high-capacitance dielectric for flexible electrowetting-on-dielectric (EWOD) applications. Unlike conventional dielectric materials such as SiO_2 and Al_2O_3 commonly used for EWOD, an ion gel offers two or three order higher capacitance than them, while being fabricated through a simple low-cost spin-coating process without complex and expensive fabrication setups such as high vaccume facilities. In this paper, a brief introduction into the constituents of the ion gel and its electrical modeling for EWOD are discussed, followed by fabrication methodologies. With the ion gel films consisting of a [P(VDF-HFP)] copolymer and a [EMIM][TFSI] ionic liquid, we compared EWOD performance of the ion gel samples with other conventional dielectric materials and showed the potential of the ion gel material capable of low-cost, spin-coatable, transferable and high-capacitanec dielectric for flexible EWOD applications.

Keywords: electrowetting-on-dielectric (EWOD), ion gel, high-κ dielectric

1 INTRODUCTION

Electrowetting-on-dielectric (EWOD) is an emerging liquid-handling technology enabling the surface tension modulation of a liquid with an applied electric field. When an electric potential is applied between a liquid and a solid electrode, the charge re-distribution modifies the surface tension at the liquid-solid interface where the like-charges repulsion decreases the work by expanding the surface area. Due to its force dominance over body forces in small scale, the technology has been widely applied. In recent years, EWOD has been attractively used for 3D flexible applications such as electronic display [1], lab on a chip [2], and biochemical sensors [3].

An EWOD phenomenon can be mathematically explained by the Young-Lippmann equation, showing the relationship between the applied electric potential (V) and is the contact angle (θ) of the droplet, given as [4]:

$$\cos\theta = \cos\theta_0 + \frac{1}{2\gamma_{LG}} cV^2 \qquad (1)$$

where θ_0 is the contact angle of the droplet with zero potential application, γ_{LG} is the surface tension between two immiscible fluids, and c is the capacitance per unit area. According to this equation, the EWOD performance can be improved by using high-capacitance dielectric materials. To meet such requirements, extensive studies have been conducted on dielectric materials that can offer a high capacitance to lower operating voltage. Several high-κ materials such as Si_3N_4, Al_2O_3, and Ta_2O_5 are typically proposed to provide a high-capacitance benefit. However, these materials need expensive and complex vacuum facilities like CDV, PECVD, and sputtering for layer deposition. Particularly for flexible EWOD applications, those conventional fabrication processes can't practically provide the rigidity of the materials. Alternatively, polymer-based materials such as PDMS, SU-8, and Parylene C have been used to permit deformability. However, a typical spin-coating method for deposition of those material yields a thick dielectric layer in the range of µm. Consequently, they offer very low capacitance requiring operational voltages as high as 700 V [3].

Here, we present, for the first time, the use of an ion gel material as a high-capacitance dielectric for flexible EWOD applications. It offers two or three order higher capacitance than conventional dielectrics such as such as Si_3N_4, Al_2O_3, and Ta_2O_5, while being fabricated through a simple low-cost spin-coating process without any expensive vacuum facilities. We successfully fabricated the ion gel films, which consist of a copolymer poly(vinylidene uoride-co-hexauoropropylene) [P(VDF-HFP)] and an ionic liquid, 1-ethyl-3-methylimidazolium bis(triuoromethylsulfonyl)imide [EMIM][TFSI], through a simple spin-coating process. Our study for EWOD performance indicates that ion gel was capable of providing an improved high-capacitance dielectric and lowering operational voltage without bubble generation by electrolysis. The deformability of ion gel was demonstrated by transferring to a flexible substrate and subsequently bending it.

2 THEORETICAL MODELING

The ion gel is a recently developed material in the form of a thin-film made of an ionic liquid and a structuring polymer. Ionic liquids (also known as room temperature molten salts) themselves have been very attractive due to their favorable properties such as a wide electrochemical

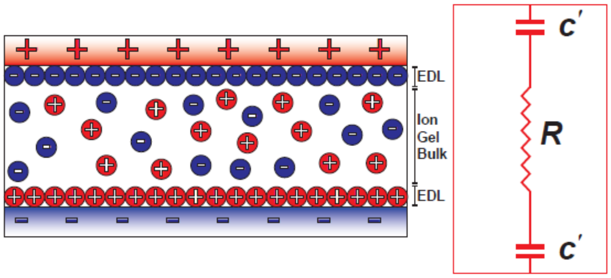

Figure 1. Schematic of the ion gel layer sandwiched between two electrified surfaces of opposite polarity (left) and its equivalent circuit model (right). Counter-ions from the gel pack themselves against their respective electrode surfaces, forming thin EDL capacitors, *c*'. In the bulk of the ion gel layer, a resistance *R* exists due to electrolyte resistance emerging from the constituent ionic liquid. At DC or a very low frequencies typically used for EWOD operation, the polymer resistance sandwiched by two capacitors can be simply negligible.

window, high thermal stability, almost negligible vapor pressure, and large ionic conductivity and capacitance. For several applications of the ionic liquid, it is desirable to utilize them in the form of a solid film. Such a thin-film form known as ion gels is attained through the addition of a structuring polymer to the ionic liquid thereby inducing either physical or chemical crosslinking.

For a fundamental study of the ion gel used for EWOD as a dielectric layer, it is first necessary to understand the nature of capacitance within ionic liquids, because they are an essential building block of the ion gel. At electrified interfaces, free counter-ions inside ionic liquids accumulate at the liquid-electrode interface and form an EDL capacitor. One of the accurate forms of measurement of this EDL capacitance of ionic liquids is obtained through the measurement of electrostatic forces normal to the ionic liquid-electrode interfaces. This approach provides an approximate EDL capacitance value in the range of 3 ~ 11 $\mu F/cm^2$ for most commonly used ionic liquids [5]. Some more studies reported that the structuring polymers used to provide a network around the ionic liquids thereby forming a solid thin-film do not contribute to the capacitance of the gel [6]. This also suggested that the high capacitance reported earlier is as a result of the EDL formation that is not influenced by the type of structuring polymer used.

Based on the studies of ion gels previously reported, the ion gel dielectric for EWOD can be modelled with an equivalent circuit as presented in Figure 1. Following its constituent ionic liquid, the ion gel also forms compact EDL layers at electrified interfaces while at the same time there is a bulk electrolyte resistance also emerging from the constituent ionic liquid. The effective capacitance of the ion gel is entirely dependent on its EDL capacitance making it overall layer thickness independent. At DC or a very low frequencies typically used for EWOD operation, the voltage consumption across the polymer resistance, which is sandwiched by two capacitors, can be simply neglected.

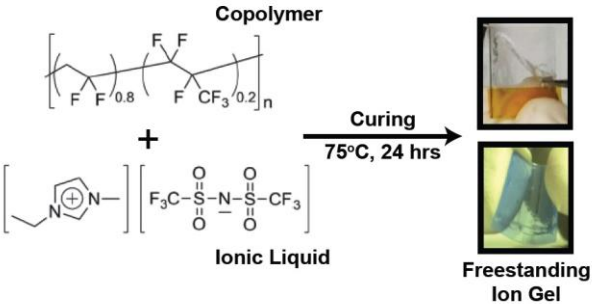

Figure 2. Chemical structures of the P(VDF-HFP) copolymer (top) and the [EMIM][TFSI] ionic liquid (bottom) which are cured to obtain free standing ion gels. The images show layers of an ion gel and Teflon fabricated on a glass substrate (right top) and then transferred on a flexible ITO substrate, which can be bent with ease (right bootom).

3 EXPERIMENTAL METHODS

We successfully obtained a spin-coatable ion gel layer for flexible EWOD applications. P(VDF-HFP) polymer was selectively dissolved in [EMIM][TFSI] ionic liquid and diluted in acetone. It was then spin-coated on an ITO substrate and cured in an oven to completely remove the solvent. The gelation process occurs when these crystals are brought together by polymer chains dissolved in the solution. Figure 2 illustrates the chemical structures of the copolymer and the ionic liquid. The layer initially fabricated on a glass wafer was transferred with the help of tweezers onto a flexible ITO substrate indicating ease of transferability.

Figure 3 graphically represents some of the different gel layers that were fabricated under various conditions. The thickness was characterized with the dry film after curing. By varying spin speed as well as the wt % ratio of the copolymer, ionic liquid and solvent, we were able to vary the ion gel thickness from 4 μm to 18 μm. Subsequently, a 6 % Teflon AF as well as 1 % Teflon AF solution were spin-coated and cured over the ion gel layer to provide a hydrophobic surface.

After the layer deposition, we conducted both static and dynamic EWOD tests to investigate the performance of the new ion gel layer. Figure 4 shows experimental setup for the static EWOD studies. A water droplet was placed on the spin-coated ion gel and Teflon layers. The thickness of the gel layer and the Teflon layer were individually varied to study their impact on the EWOD performance. A platinum (Pt) probe was inserted into the droplet while the buried ITO electrode was grounded. Voltage was then applied between the probe and the ground using a low voltage DC source controlled by LabVIEW. The contact angle was then measured at incremental voltages in steps of 5 V.

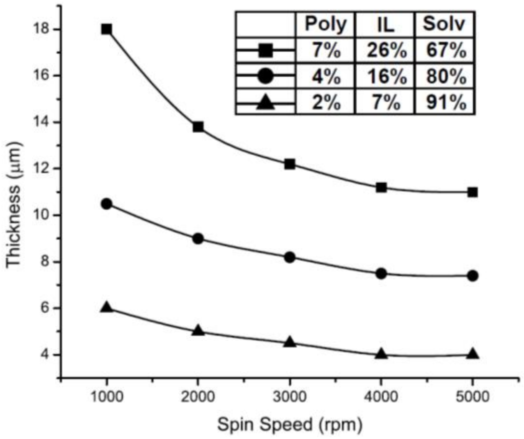

Figure 3. Various thicknesses of an ion gel layer fabricated by varying spin speed and relative wt % of the mixtures. The legend indicates the relative wt % ratio of the copolymer P(VDF-HFP), the ionic liquid [EMIM][TFSI], and the acetone solvent.

4 RESULTS AND DISCUSSION

First, static EWOD tests were performed to benchmark the performance of the ion gel against certain standard dielectrics commonly used in EWOD. This would help gauge the practicality of its usage in various EWOD applications. Al_2O_3 was chosen to represent standard thin-film dielectric materials deposited through atomic layer deposition (ALD) processes that typically require expensive high-vacuum facilities. In contrast, PDMS was chosen to represent dielectric materials fabricated by a simple spin-coating procedure specifically used for flexible EWOD applications. The thickness of the ion gel was 10 μm, while that of Al_2O_3 and PDMS were 100 nm and 10 μm respectively. Teflon layer of the same thickness (170 nm) was spin-coated on the above mentioned dielectrics for comparison.

Figure 5 shows that the gel layer performs much better than other benchmarked dielectrics with a given thickness of a Teflon layer. As expected, EWOD performances are shown in the order of Al_2O_3 and PDMS, which is the same order of their capacitance magnitudes. One interesting observation was that electrolysis occurs on the Al_2O_3 sample at 55 V (see the inset (c)), while no such phenomena occurs in the case of the ion gel (see the insets (a) and (b)) even at the saturation voltage around 50 V. This implies that dielectric layers deposited at such small thicknesses may not be very practical for use in microfluidic devices that require higher voltages, while the ion gel which offers a thickness independent capacitance can be simply spin-coated on patterned electrodes for robust usage in microfluidic applications. Additionally, being a high capacitance material, the ion gel induces large electrostatic storage energy within the hydrophobic and dielectric stack which is in turn crucial for large surface tension modulation. This again is evident from the theoretical study in Eq. (1), which is verified by our experimental results in Figure 5.

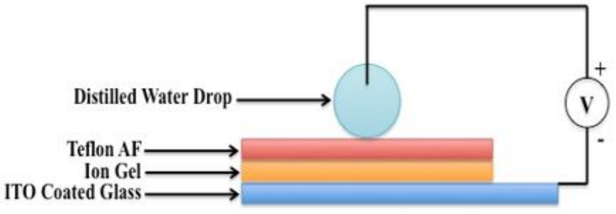

Figure 4. Experimental setup for static EWOD study. A 5 μL distilled water droplet is loaded on top of the hydrophobic (Teflon AF) and dielectric (ion gel) layers.

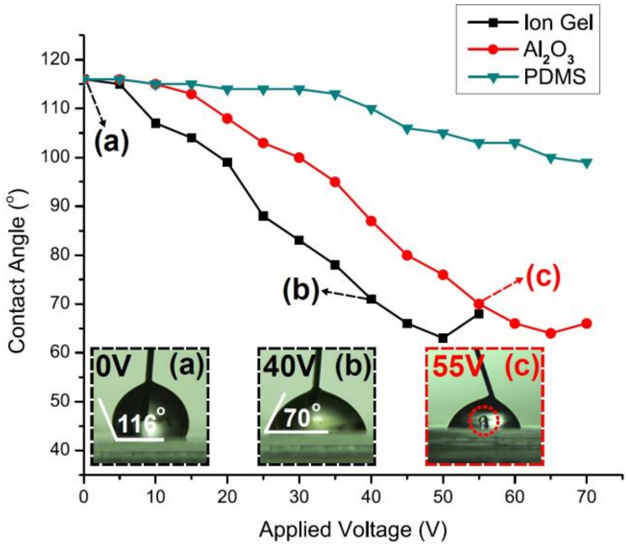

Figure 5. A comparative study of the EWOD performance of the ion gel versus Al_2O_3 and PDMS. Al_2O_3 was chosen to represent standard thin-film dielectric materials used in EWOD while PDMS was chosen to represent dielectric materials requiring a simple fabrication procedure. Insets (a) and (b) display images of a 5 μL water droplet over the Teflon / ion gel stack at 0 V and 40 V respectively. Inset (c) displays an image of the water droplet over the Teflon / Al_2O_3 stack at 55 V where electrolysis is clearly observed (circled in red).

We also studied the droplet actuation phenomena using the novel ion gel dielectric. For the experiments, an electrode pattern was created through standard photolithography processes using AZ P4260 photoresist spin-coated on an ITO coated substrate. The pattern was then wet etched using 37% concentrated HCl for 4 minutes. The photoresist was then stripped using acetone to realize the electrode pattern. Over the pattern, a 15 μm ion gel layer and an 880 nm Teflon AF layer were deposited and cured to complete the fabrication of the device. Figure 6 shows the movement of a 10 μL water droplet at a speed of 17.5 cm/sec on the Teflon / ion gel

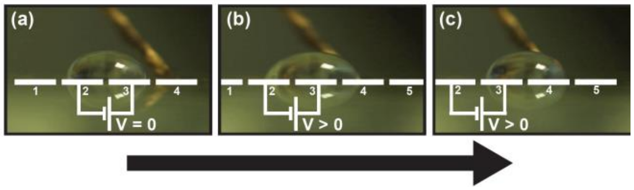

Figure 6. EWOD based droplet movement was demonstrated using the novel ion gel dielectric. Some of the electrodes in the series are labeled from 1 to 5. The speed of the droplet was measured as 17.5 cm/sec

coated substrate. Some of the electrodes in the series are labeled from 1 to 5. The droplet was initially over electrode 2 and 3 and there was no applied potential (Figure 6a). DC voltage of 100 V is applied between electrode 2 and 3 realizing droplet actuation (Figure 6b). When the voltage is released at Figure 6 (c), the droplet has moved forward and now covers electrodes 3 and 4. This process is repeated iteratively to achieve droplet movement.

5 CONCLUSION

A novel ion gel capable of spin-coatable, transferable and high-capacitance dielectric was studies for flexible EWOD applications. At electrified interfaces, a large number of free counter-ions inside ionic liquids tightly accumulate at the liquid-electrode interface and form an EDL. Such thin but highly-densified ion distributions allow to hold large electrostatic energy across the EDL capacitor and hence large surface tension modification necessary for the improved EWOD performance. It was reported that the gel layer can provide a few order higher capacitance than that of conventional dielectric materials commonly used for EWOD. The fundamental study of the ion gel material interestingly indicates that the capacitance is thickness independent. This suggests that a relatively thick ion gel over 10 µm can be used to provide a stable high-capacitance dielectric property without the layer breakdown (i.e. electrolysis) for wide EWOD applications.

The ion gel films, which consist of a copolymer poly(vinylidene uoride-co-hexauoropropylene) [P(VDF-HFP)] and an ionic liquid [EMIM][TFSI], 1-ethyl-3-methylimidazolium bis(triuoromethylsulfonyl)imide, was succefully fabricated through a simple spin-coating process without expensive high-vacuum facilities that are typically required conventional IC fabrication processes. It was further transferred to flexible ITO substrates and demonstrated the deformability of the ion gel dielectric by subsequently bending it. The ion gel's EWOD performance was compared with certain commonly used dielectric materials for traditional as well as flexible EWOD and experimentally showed the lower operation voltage at a given contact angle modulation on ion gel samples. Finally, we also demonstrated droplet movement at a speed of 17.5 cm/sec on the Teflon / ion gel coated substrates.

The paper informs that an ion gel is capable of lowering operational voltage and providing an improved high-capacitance dielectric without bubble generation by electrolysis. With its relatively large capacitance and easy fabrication, the ion gel is seen as a material with great potential for 3D flexible EWOD applications.

REFERENCES

[1] D. Y. Kim and A. J. Steckl, “Electrowetting on paper for electronic paper display," ACS Appl. Mater. Interfaces, 2, 3318-3323, 2010.

[2] S.-K. Fan, H. Yang, and W. Hsu, “Droplet-on-a-wristband: Chip-to-chip digital microfuidic inter- faces between replaceable and exible electrowetting modules," Lab Chip, 11, 343-347, 2010.

[3] M. Abdelgawad, S. L. S. Freire, H. Yang, and A. R. Wheeler, “All-terrain droplet actuation," Lab Chip, 8, 672-677, 2008.

[4] M. G. Lippmann, "Relations entre les phénomènes electriques et capillaires," Annales de Chimie et de Physique, vol. 5, pp. 494-549, 1875.

[5] J. H. Cho, J. Lee, Y. Xia, B. Kim, Y. He, M. J. Renn, T. P. Lodge, and C. D. Frisbie, “Printable ion-gel gate dielectrics for low-voltage polymer thin-film transistors on plastic," Nat. Mater., 7, 900-906, 2008.

[6] S. Zhang, K. H. Lee, C. D. Frisbie, and T. P. Lodge, “Ionic conductivity, capacitance, and viscoelastic properties of block copolymer-based ion gels, Macromolecules, 44, 940949, 2011.

[7] K. H. Lee, M. S. Kang, S. Zhang, Y. Gu, T. P. Lodge, and C. D. Frisbie, “Cut and stick" rubbery ion gels as high capacitance gate dielectrics," Adv. Mater., 24, 44574462, 2012.