Review of: "Circadian humidity fluctuation induced capillary flow for sustainable mobile energy"

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The paper by Tang et al. (2022) uses the circadian humidity fluctuation induced capillary flow to generate electricity. A well-shaped fluid drop of ionic liquid (1-Octyl-3-methylimidazolium chloride) was selected by the authors owing to its large moisture absorption/desorption capability on exposure to atmosphere. The drop is fixed on a polydimethylsiloxane nanowire array with known contact angle. Electrodes are placed at centre and edge of the drop to collect the open circuit voltage. The authors hypothesize that moisture absorption/desorption within IL (ionic liquid) drop causes directional flow along solid/liquid interface and such a flow induces a potential difference from ion re-distribution. The authors validate their hypothesis by in-situ microscope imaging and conduct experiments to illustrate how environmental humidity affects flow rate and power generation performance. When the water content (WC) of the IL drop is less than its saturated water content (WC_s), moisture is adsorbed from the surroundings with peak power output of 110 mV. Adsorption of water vapor induces flow of hydrated ions towards the centre to remove excess liquid from the perimeter. The opposite phenomenon occurs when the wet IL drop undergoes desorption.

Moisture sorption by ionic liquids occurs by (1) adsorption of water molecules on the IL surface, 2) their absorption inside the IL by diffusion and 3) formation of water-ion complexes (Di Francesco et al. 2011). Bulk of sorbed water is retained inside IL as 1:2 hydrogen bonded, anion...HOH...anion complexes (Cammarata et al. 2001; Cao et al. 2012).
The diurnal variations in relative humidity (RH) are a function of geographical location and season. The absolute variation of RH is typically about 20% at any given level of altitude along the day (Chepfer et al. 2019). At a given geographical location, $RH_{atmosphere}$ can be expected to be lower than RH_{IL} during mid-day (lowest RH of atmosphere)forcing moisture loss from IL by dehydration of the anion...HOH...anion complexes. Conversely, during mid night to early morning, the $RH_{atmosphere}$ is expected to be > RH_{IL}, causing moisture sorption by IL.

Moisture loss would create WC < WC_s condition inside the IL from the ionic liquid-atmosphere interaction. Simultaneously, the suction created inside the unsaturated IL by moisture loss would reduce the separations between ion complexes. Magnitude of the suction (ψ) generated at WC < WC_s condition can be obtained as (Fredlund et al. 2012):

$$\psi = \frac{2T}{r} \cos \alpha$$

(1)

In equation 1, T is the surface tension of the liquid, r is the radius of capillary pore between adjacent ion complexes, and α is the contact angle between menisci and wall of the pore. Narrower pores and greater suction is facilitated as the IL dehydrates. The magnitude of suction generated at given RH is obtained from Kelvin's equation (Fredlund et al. 2012) as:

$$\psi = -\frac{RT}{v_w} lnRH \; (2)$$

In equation 2, u_w is the partial molar volume of liquid water, RH represents the relative humidity, R is the universal gas constant (8.314 J/mol.K) and T (K) is the absolute temperature. Equation 2 indicates that suction inside IL approaches zero at WC = WC_s (saturated) condition. As the RH inside IL reduces to 90% (WC < WC_s unsaturated condition) the suction inside IL increases to 14 MPa (T =293 K). Upon further dehydration to 70% RH, the suction inside IL increases to 48 MPa (T = 293 K). Only a fraction of suction generated at given RH (represented as χψ; where χ is a material parameter related to degree of saturation) participates in forcing the ion complexes together during the dehydration process. The value of χ in soils ranges from 0 (WC/WC_s = 0) to 1 ((WC/WC_s = 1) (Fredlund et al. 2012).

There is evidence that dehydration of negatively charged clay particles (<2 μm) by moisture loss causes their aggregation that in turn reduces their water absorption capacity (Rao et al. 1989). Suction stresses generated during drying facilitate small interparticle separations that can overcome mutual repulsion between like charged particles. Strong van der Waals' and Coulombic bonds develop between the charged particles at very close separations and are not easily reversed. The resultant aggregation reduces the available surface area for interaction with moisture.

Guided by the observations with negatively charged clay particles, long-term cyclic dehydration-hydration of IL may create bonding between ion complexes and the reduced area may lower the hydration ability of ionic liquids. Tang et al. (2022) have demonstrated power generation from circadian humidity fluctuation for their set up to 3 days, which was a marked improvement over previous results. A much longer response of IL to circadian RH fluctuations to rule out possible decay in power generation from re-structuring of ionic complexes merits investigation.

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