Supporting Information

“Ionic Liquids Based Vibration Energy Harvester by Periodically Squeezing Liquid Bridge”

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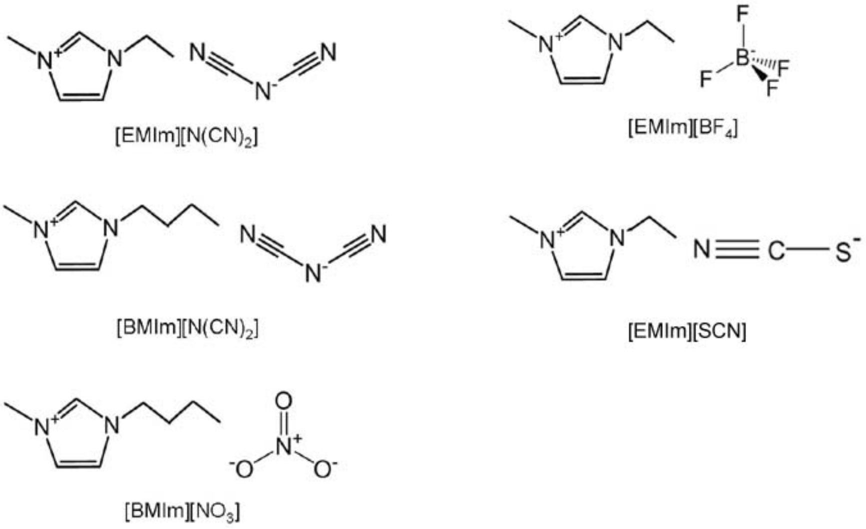
1. Structure and Characterization of Ionic Liquids

Five imidazolium ionic liquids with different cation and anion structures (Fig. S1), namely, 1-ethyl-3-methylimidazolium dicyanamide ([EMIm][N(CN)$_2$]), 1-butyl-3-methylimidazolium dicyanamide ([BMIm][N(CN)$_2$]), 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm][BF$_4$]), 1-ethyl-3-methylimidazolium thiocyanate ([EMIm][SCN]) and 1-ethyl-3-methylimidazolium nitrate ([BMIm][NO$_3$]), were synthesized in our laboratory according to the established procedures.



[EMIm][N(CN)$_2$]

[EMIm][BF$_4$]

[BMIm][N(CN)$_2$]

[EMIm][SCN]

[BMIm][NO$_3$]

Figure S1. Formulas and structures of the ionic liquids studied.

Table S1. Viscosity, conductivity, surface tension and density of liquid media.

Liquid media	Viscosity/cP	Conductivity/mS cm^{-1}	Surface tension/mN m^{-1}	Density/g cm^{-3}
H_2O	1	1.94E-2	71.2	0.997
[EMIm][N(CN)$_2$]	21	28.00	47.3	1.230
[BMIm][N(CN)$_2$]	27	9.74	37.8	1.026
[EMIm][BF$_4$]	45	14.00	49.0	1.280
[EMIm][SCN]	22	13.07	57.8	1.117
[BMIm][NO$_3$]	168	2.04	44.6	1.174

Table S1 shows the physical parameters of the compounds studied in this paper. All the data were got at 25±2 °C. Prior to measurements all ILs were dried in vacuo at 80 °C for 3 hours, except [EMIm][N(CN)$_2$] and [BMIm][N(CN)$_2$], which dried in vacuo at 60 °C for 5 hours. The water content was ~226 ppm for [EMIm][N(CN)$_2$], ~206 ppm for [BMIm][N(CN)$_2$], ~287 ppm for [EMIm][BF$_4$], ~163 ppm for [EMIm][SCN] and ~160 ppm for [BMIm][NO$_3$].

The viscosity was measured on a Brookfield DV-III+ viscometer (Brookfield, Middleboro, Massachusetts). The ion conductivity was measured using a Mettler-Toledo Seven Muliti meter. The surface tension was measured on a surface/interface analytical device (Solon Tech. , Shanghai) using the Du Noüy ring method. The water content was measured by Karl-Fisher analysis (Metrohm KF coulometer).

2. EVH Fabrication and Assembly

The surface of the top plate was coated with thin hydrophobic layer using dip-coating method. The ITO glass was immersed in a 2% (w/v) of Teflon AF 1600 (DuPont) in FC 75, and then withdrawn from the solution at a constant speed of 750 μm/s. The Teflon-covered ITO glass was heat-treated at 180 °C for 30 minutes, in order to remove residual solvent and improve the adhesion of the Teflon layer to the substrate, which given a very thin Teflon coating (~ 400 nm, ε_r=1.93) as a top layer to obtain the desired hydrophobic and low hysteresis properties. The bottom plate was ITO glass, which is hydrophilic. The images of a 15 μL [EMIm][BF$_4$] droplet on ITO (bottom plate) and Teflon-coated ITO (top plate) are shown in Supplementary Figure S2. The contact angles are 72° and 105°, resepectively, which demonstrate the hydrophilic (bottom plate) and hydrophobic (top plate) properties. Then ionic liquid (~15 μL) was injected onto the bottom plate through a 10 μL syringe.

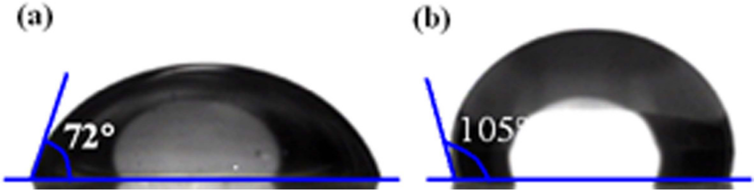


Figure S2. A 15 μL [EMIm][BF$_4$] droplet on ITO (bottom plate) (a) and Teflon-coated ITO (top plate) (b).

The bottom plate was actuated using a electrodynamic shaker (JZQ-2, XLZD Inc.), which was driven by function generator (TFG2030G, SUING Inc.) through power amplifier (GF-20, XLZD Inc.). The vibration amplitude L was measured by a vibration measuring instrument (XD-8, XLZD Inc.) using accelerometer installed on the vibrating surface. The exact position of the top electrode was precisely controlled by electric displacement platform connected to precision uniaxial motion controller (7SC301, Beijing 7-s optical instruments Inc.). The voltage drop V_L across the resistive load R_L was recorded by LabVIEW 2011 with data acquisition board (NI-USB-6210 DAQ) connected to computer.

Temperature was controlled by Peltier junction connected to constant current power supply (CB3005DG, CZB Inc.).

3. Electric Circuit Model

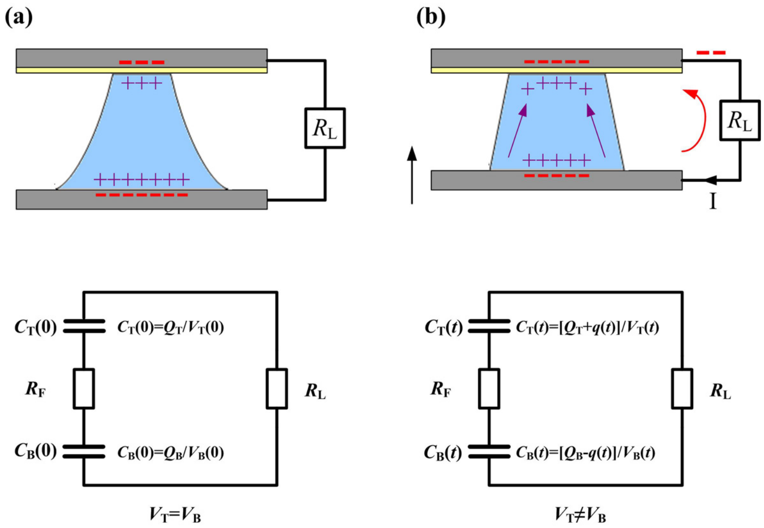


Figure S3. The corresponding equivalent electrical circuits (a) when the height of liquid bridge is fixed with time (equilibrium state) and (b) at the very moment when the height of liquid bridge is decreasing (non-equilibrium state)

According to the circuit model in reference [1], the electric circuit is shown in Supplementary Fig. S3. It includes two variable capacitors and two resistor. Fig. S3(a) is the electrical circuit when the liquid bridge is in equilibrium state after a long time with stationary bottom plate (no vibration). Because of the fully relaxed system, $V_T=V_B$ and no current flows. At the very moment when the two plates are approaching each other immediatedly after the vibration commences at t=0, the top electrical double layer capacitor (EDLC) C_T is increasing and the bottom EDLC C_B remains constant. This process results in the movement of charge between two capacitors until $V_T=V_B$. The behavior of this electrical circuit can be theoretically described by using the following differential equation [1]:

$$(R_F + R_L)\frac{dq(t)}{dt} = V_B(t) - V_T(t)$$
$$= \frac{Q_B - q(t)}{C_B} - \frac{Q_T + q(t)}{C_T(t)}$$

$$q(t=0) = 0 \tag{S1}$$

Where C_T and C_B are the capacitances of variables capacitors, V_T (Q_T) and V_B (Q_B) are the voltages (charges) on C_T and C_B, respectively, and $V_T=Q_T/C_T$, $V_B=Q_B/C_B$, R_F and R_L are resistances of the liquid bridge and load, $q(t)$ is the increment (decrement) of charge in the top (bottom) EDLC at time t. Variation of capacitances with time can be approximated as:

$$C_T(t) \cong \frac{\varepsilon_0 \varepsilon_p}{d} A_T(t) \tag{S2}$$

$$C_B(t) \cong \frac{\varepsilon_0 \varepsilon_d}{\lambda_D} A_B(t) \cong \text{constant} \tag{S3}$$

Where ε_0 is the vacuum permittivity, ε_d and ε_p are the relative permittivity of the ILs and the

Teflon, respectively, $A_T(t)$ is contact area between the liquid bridge and top plate with time, $A_B(t)$ is contact area between the liquid bridge and bottom plate with time, d is the thin film dielectric thickness, λ_D is the thickness of the electrical double layer.

If the height of liquid bridge is oscillating with frequency f, two EDLCs continuously charge and discharges with different phases relative to each other, which generates the AC electrical current. The voltage drop on load R_L is $V_L(t)=\triangle V(t)R_L/(R_F+R_L)$, where $\triangle V(t)\equiv V_B(t)-V_T(t)$. The voltage drop $V_L(t)$ was captured by the data acquisition board and converted into electrical current allowing direct calculation of the generated power as a function of time.

4. Numerical Calculations

The numerical calculations of voltage drop V_L(t) were carried out with Matlab software based on equations (S1)-(S3). The parameter values of Fig. 2 in main text are as follows:

The initial contact area $A_T(0)$ is about 9.8 mm^2, the contact areas $A_B(t)$ is nearly constant due to the small contact angle and pinning effects, is about 17.2 mm^2, the variation of contact area $A_T(t)$ is approximated by the function $A_T(t)=9.8+5.0\sin(20\pi t)$ mm^2, the relative permittivity ε_p and ε_d are about 1.93 and 11.0 [2], respectively, the thin film dielectric thickness d is about 400 nm, the Debye length λ_D is about 0.5 Å [3], the conductivity of [EMIm][N(CN)$_2$] is 28.00 mS cm^{-1} and the initial height of liquid bridge is about 1.5 mm, so the resistance of the liquid bridge R_F is about 40 Ω, and the charges stored on top EDLC C_T is about 0.41 nC.

The parameter values of Fig. 4 in main text are the same as above except for the variable.

5. Other Experimental Result

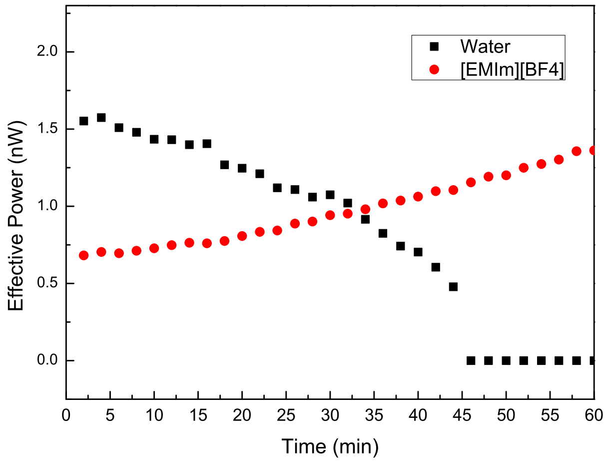


Figure S4. Effective power outputs with time of the 15 µL water and [EMIm][BF$_4$] bridge in air. Here, L=0.35 mm, f=10 Hz and R_L=30 MΩ. Because the [EMIm][BF$_4$] absorbed water from air, the output power increased slowly.

References

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