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## Mechanical-to-Electric Energy Conversion by Mechanically Driven Flow of Electrolytes Confined in Nanochannels

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This letter presents a conceptual mechanical-to-electric energy harvesting mechanism, in which an electrolytic flow is driven through a nanoporous electrode to perturb the interfacial electrochemical equilibrium and generate voltage. Using an electrochemical analysis coupled with molecular simulations, we demonstrate that both flow velocity and nanopore size have prominent effects on the structural and electrochemical properties of nanoconfined electrolytes. By first-order approximation, the energy conversion efficiency is found to be promising, and strategies for further improvements are suggested. A preliminary experiment is carried out to validate that the electrolytic flow in nanopores can cause significant energy generation. © 2013 The Japan Society of Applied Physics

arvesting mechanical energy from ambient sources<sup>1)</sup> is promising to provide sustainable power for lowpower portable electronic devices,<sup>2)</sup> wireless sensors,<sup>3)</sup> and medical implants<sup>4)</sup> to remove or alleviate the requirement for battery replacement. The technological challenge hinges upon the mechanical-to-electric energy conversion mechanism. Many studies have focused on piezoelectric materials,<sup>5–8)</sup> but they are known to have low strength and/or low throughput.<sup>9)</sup> More efficient and robust mechanical-to-electric conversion mechanisms may be achieved by operating aqueous solutions in nanoconfinements. The intriguing interfaces between aqueous solutions and carbon materials have enabled a number of applications related with the modulation of electrical field in nanoconfined environments.<sup>10-13)</sup> Carbon supercapacitors have shown extremely high capacitance when the nanopore size is reduced below 1 nm. The increased capacitance contradicts classic theories, and has been attributed to the partial removal of the hydration shell in nanoconfinements.<sup>11)</sup> On the other hand, graphene field effect transistors have been demonstrated to be effective in the electrical detection of inorganic<sup>13)</sup> and biochemical<sup>12)</sup> analytes. By applying an electrical field, ions build up at the material interfaces and induce holes and electrons by capacitive charging, thus varying the conductance of the nanochannel.<sup>12)</sup>

These applications of nanofluidics-based material systems are critically dependent on the structure and dynamics of electrolytes confined in nanochannels. Nanoconfined electrolytes feature unique molecular, energetic, and flow characteristics, including an incomplete hydration shell,<sup>14)</sup> slow ionic diffusion,<sup>15)</sup> energetically unfavorable infiltration,<sup>16)</sup> and uneven ionic polarization.<sup>17)</sup> Of particular interest is the interfacial electrochemical characteristics. In nanoconfinements, opposite solid planes get so close that the Helmholtz and Gouy-Chapman layers residing in the vicinity of both solid surfaces are strongly interfered with and distorted. Partially due to these reasons, both simulation<sup>18)</sup> and experiment<sup>19)</sup> have shown that increasing the charge density on a solid surface that confines an electrolytic solution can increase the thickness and the counter-ion density in the electric double layer (EDL); however, charge inversion cannot



**Fig. 1.** Schematic illustration of the nanofluid-based mechanical-toelectric energy conversion mechanism: as the piston is driven to move by external mechanical excitations, an electrolyte solution is forced to flow through a nanoporous electrode. The confined electrolytic flow varies the cross-interface electric potential,  $\phi$ , and generates a voltage V between the nanoporous electrode and a reference electrode residing in the bulk electrolyte solution.

occur even at high surface charge densities. To correlate structural properties with electrical properties, Poisson-Boltzmann theory has been adopted in a previous study to compute the electrostatic potential across the interface between functionalized solid monolayers and electrolytes.<sup>20)</sup> However, the effect of flow velocity on the interfacial electrical potential has been relatively underexplored, which represents ample opportunities for harvesting ambient mechanical energy.

This work investigates a conceptual mechanical-toelectric energy conversion mechanism that involves two electrodes immersed in an electrolyte solution. As illustrated in Fig. 1, under external excitations, the electrolyte solution can be forced to flow through the nanoporous electrode in a controlled manner. According to classic electrochemistry, the formation of EDL in nanopores may induce an electric potential difference,  $\phi$ , across the solid-fluid interface.

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Importantly,  $\phi$  is not only a function of adopted materials, but it also strongly depends on the environment in which the liquid-solid biphase system is operated. Different flow velocities and temperatures can perturb the interfacial electrochemical equilibrium to different extents, thus varying  $\phi$ . By connecting such a biphase system with a reference electrode residing in the bulk liquid phase, a voltage can be generated due to the different  $\phi$  at the two electrodes. The electric output is sustainable if the flow velocity is continuously varied by external mechanical inputs, which is compatible with most ambient mechanical energy sources. Since this mechanism is based on interfacial electrochemistry that can be amplified by increasing interfacial areas, nanoporous materials with the pore size ranging from subnanometer to hundreds of nanometers are considered in this study. Note that the present mechanism is radically different from the well-known streaming potential. The latter is generated by an electrolytic flow through a charged channel and the direction of potential is along the flow direction; in the present mechanism, however, the electric potential difference is perpendicular to the flow direction.

An electrochemical analysis coupled with molecular simulations is employed to investigate the effects of flow velocity and nanopore size on the interfacial electrochemical properties of nanoconfined electrolytes. We consider a 12 wt % aqueous solution of NaCl and four nanopores modeled as carbon nanotubes (CNTs) with different diameters D = 8.14, 13.56, 20.34, and 27.12 Å. Classical molecular dynamics is adopted to simulate the flow of the solution at various velocities through the model nanopores. Due to the viscosity of electrolytes,<sup>21)</sup> a driving force (e.g., pressure drop as adopted in this study) is required to drive the fluid flow. The periodic boundary condition is applied in the axial direction. The temperature is fixed at 300 K. In order to rule out possible influences of initial molecular configurations, 50 initial configurations are sampled for each case and independently simulated. All results shown below are averaged from these sampled systems.

Based on the radial density distributions of the four particles (Na<sup>+</sup>, Cl<sup>-</sup>, O, and H) obtained from simulations, pointwise charge density can be readily assessed as  $\rho_{\rm C} =$  $\sum_{i=1}^{n} \rho_i \cdot C_i$  where *n* represents the number of species (*n* = 4) in this study),  $\rho_i$  denotes the density of the *i*th species, and  $C_i$ represents the charge carried by the species. The resulting  $\rho_{\rm C}$ is further correlated with the electric potential,  $\varphi$ , by solving a Poisson's equation,  $\nabla^2 \varphi = -\rho_{\rm C}/\varepsilon_0 \varepsilon$ , where  $\varepsilon_0$  and  $\varepsilon$  are the vacuum permittivity and the dielectric constant of the medium, respectively. In this study,  $\varepsilon$  is assumed to be the same as that of the bulk 12 wt % aqueous solution of NaCl (about 44.30),<sup>22)</sup> despite the fact that the dielectric constant could be varied at material interfaces.<sup>23)</sup> The computation yields a radially varying electric potential,  $\varphi(r)$ . By taking the difference between  $\varphi$  at the solid surface and that at the center of the confined liquid column, a cross-interface potential difference,  $\phi = \varphi|_{r=R} - \varphi|_{r=0}$ , is deduced with R denoting the pore radius.

Since the adopted model nanopores are just a bit larger than the interatomic equilibrium distance, only a few ions and atoms can be simultaneously accommodated in the same cross section of the nanopore [insets of Figs. 2(a)-2(d)]. Figure 2 plots the radial density distribution (RDD) for all

the four particles. H and O atoms are highly concentrated close to the solid surface, while  $Na^+$  and  $Cl^-$  show very low densities in the same region. Given the high density of water and low densities of ions in the first solvation shell [i.e., FSS, the first shell of concentrated water from the solid surface, as illustrated in Fig. 2(b)], the ionic hydration is significantly varied within the nanoconfinement.

Figure 3(a) plots the cross-interface potential difference,  $\phi$ , for four model nanopores when the confined nanofluid remains stationary. As the size of the confinement decreases,  $\phi$  is shown to first ascend, attaining the maximum of 38.04 mV at D = 13.56 Å, and then drops to 3.61 mV when the pore size is reduced to 8.14 Å. The sudden drop of  $\phi$  in the sub-nanometer nanopore is partially attributable to the unique (single-file) molecular and ionic structures.<sup>14</sup>

The value of  $\phi$  also strongly depends on the flow velocity. Theoretically, different ions/atoms in a nanoconfined electrolyte solution have different affinities with the solid surface atoms. When the solution is driven to flow, particles with higher mobility are given higher probabilities to leave their equilibrium radial positions, while those with lower mobility are more likely to stay. The re-equilibrized interface strongly affects  $\phi$ . Figure 3(b) illustrates the effect of flow velocity on the interfacial potential difference,  $\phi$ . When v is below 125 m/s,  $\phi$  is shown to increase almost linearly with v at  $d\phi/dv \approx 0.003$  mV s/m; when v is above 125 m/s,  $d\phi/dv$  is raised to about 0.016 mV s/m. Such a nonlinear flow rate effect is attributable to the nonlinear response of the confined electrolyte to the flow velocity.

A voltage ( $V_c$ ) can be generated by connecting the solid surface with a reference electrode residing in the bulk electrolyte solution (Fig. 1). Charges are driven to move from the nanoporous electrode with relatively higher electric potential to the reference electrode with lower electric potential. However, if the confined electrolyte flow speed is constant, the system is equivalent to a nanocapacitor in which charges will eventually drain, and the voltage,  $V_c$ , is a transient peak voltage before the nanocapacitor discharges. In order to maintain its powering capability, one has to force the confined electrolyte to flow at a varying velocity. By doing so, the interfacial electrochemical equilibrium is continuously perturbed, leading to a sustainable charging and discharging process.

By first-order approximation, the output electric energy scales with  $W_{\text{out}} = \Delta V_c Q / \Delta t$ , where Q denotes the line density (along pore/flow axis) of the excessive charge residing in the FSS, and  $\Delta V_c$  is a change in the transient peak voltage caused by a velocity change of  $\Delta v$  over a time period of  $\Delta t$ . Assuming a constant acceleration of a,  $\Delta t = \Delta v/a$  and  $W_{\text{out}}$  becomes  $\Delta V_c Q a / \Delta v$ . An external mechanical energy is required to provide inertia force and to overcome surface friction while the confined liquid column is accelerated. Its power can be estimated by  $W_{\rm in} = (ma + f)v_{\rm avr}/2$ , where m and f denote the mass and friction of a confined liquid column of unit length along the pore axis, and  $v_{\rm avr}$  is the average velocity during the acceleration. Then, the efficiency of the present system can be assessed as  $\xi = 2\Delta V_c Qa/(ma+f)v_{avr}\Delta v$ . Apparently, low surface friction is desired, which may be achieved by using nanoporous materials with smoother and nonpolar solid surfaces. For simplicity, we assume f = 0 for CNTs

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**Fig. 2.** Radial distribution of the four species of atoms and ions (O, H, Na<sup>+</sup>, and Cl<sup>-</sup>) in an aqueous solution of NaCl confined statically in a nanopore with diameter D = (a) 8.14, (b) 13.56, (c) 20.34, and (d) 27.12 Å. Insets are snapshots of the confined atoms and ions (red spheres: O; white spheres: H; purple spheres: Na<sup>+</sup>; green spheres: Cl<sup>-</sup>). The number density is defined as the number of a certain type of ion/atom in a unit volume. Only half the r-z plane is plotted, where r denotes the radial direction and z is the axial direction.



Fig. 3. (a)  $\phi$  versus R for a NaCl solution statically confined in four carbon nanopores. (b)  $\phi$  versus v in a nanopore with D = 20.34 Å.

(because f of CNTs is known to be ultra-low<sup>24</sup>) and  $\xi$  becomes  $(\Delta V_c/\Delta v)(2Q/mv_{avr})$ . With the ratio of  $\Delta V_c/\Delta v$  obtained from Fig. 3(b), and both Q and m extracted from simulations, the mechanical-to-electric energy conversion efficiency is estimated to be a promising value of 5% for the system with D of about 2 nm. To further improve the energy conversion efficiency, the system should incorporate electrolytes with higher ion concentrations and lower mass densities, nanoporous materials with less surface variations, and be operated at a low  $v_{avr}$  while being accelerated fast enough (e.g., through vibration) to achieve prominent flow effects on interfacial electrochemical properties.

To validate the proposed concept, an experiment was carried out by using nanoporous monel electrodes. A tight-fitting nanoporous monel rod was inserted into a relatively small polypropylene (PP) tube (outer diameter: 9.5 mm), while another similar monel electrode was placed in a larger PP tube (outer diameter: 19 mm). For both electrodes, the nanopore size was around 200-800 nm, with the specific pore volume of about  $0.15 \text{ cm}^3/\text{g}$ . Details of material preparation can be found elsewhere.<sup>25,26)</sup> A piping system was formed by connecting the two PP tubes via a reducer. The length of the two monel rods was 19.1 mm, and they were separated by 50 mm. By using a MasterFlex L/S 7518-10

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digital drive, a 15 wt % aqueous solution of NaCl was driven to flow through the two tubes in series. The flow rate was controlled in the range from 5 to 50 ml/min. The two monel electrodes were connected by an external resister,  $R_0 = 500$ k $\Omega$ , with the voltage, V, measured using a National Instruments 6936E data acquisition (DA) system. The measurement devices were connected via platinum (Pt) wires.

Immediately after the electrolyte solution started to flow, a voltage of around 31–33 mV was measured, and the efficiency of energy conversion was measured to be on the same order of theoretical predictions. Note that the present experiment and theoretical analysis can only be qualitatively compared, mainly because of the difficulty of incorporating all practical factors such as material composition, pore structure, pore size distribution, and surface treatment into the modeling. Nevertheless, the experimental and theoretical investigations both demonstrate the effectiveness of the mechanical-to-electric energy conversion mechanism. Further experiments and theoretical verifications are being performed to characterize the system's transient behaviors for better understanding and optimization of the system performance.

To summarize, this work investigates a conceptual mechanical-to-electric energy conversion system based on a flow-rate-sensitive surface electrification mechanism. When an electrolyte solution is controlled to flow through a nanoporous electrode, different flow velocities invoke different levels of mobility of the ions and atoms, leading to considerable changes in the interfacial ionic and molecular structures along with the cross-interface electric potential difference. The findings are validated by an experiment by which the working concept is directly illustrated. A firstorder approximation of energy conversion efficiency shows that the present system has a promising efficiency in addition to a few other advantages. Further system optimization may be achieved by adopting better combinations of nanoporous materials and electrolytes with maximized flow-responsive interfacial, structural, and electrochemical changes, maximized density of surface-adsorbed charges, and minimized efforts to accelerate the electrolytic flow through nanopores. **Acknowledgments** This work was sponsored by the National Natural Science Foundation of China (11172231), the World Class University program through the National Research Foundation of Korea (R32-2008-000-20042-0), DARPA (W91CRB-11-C-0112), and the National Science Foundation (CMMI-0643726). L.L. acknowledges financial support from Utah State University and the Space Dynamics Lab.

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