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Short communication

Mechanoelectricity of a nanoporous monel–electrolyte solution system

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Abstract

The electrification of an electrolyte solution in a nanoporous alloy is investigated through a mechanoelectricity measurement experiment. As the liquid flows across the nanoporous electrode, charge separation occurs over the large nanopore surface, resulting in a significant output voltage, which is in-phase with the actuator motion. This phenomenon is different from the conventional streaming current effect, since the solid phase is conductive and no voltage can be developed along its surface.

Keywords: Nanoporous; Mechanical-to-electric energy conversion; Liquid electrification; Monel

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1. Introduction

Since the era of Benjamin Franklin and Michael Faraday, it has long been noticed that as a liquid and a solid are placed together they can be electrified spontaneously, due to the difference in attraction forces to charge carriers across the interface [1]. In the liquid phase, about 0.5 to a few nanometers away from the solid surface, there is an outer Helmholtz plane (OHP) of a high solvated ion density [2,3], as depicted in Fig. 1. Outside the OHP, the ions distribute in thermal disarrays. In the solid phase, there are counter charges. As a result, an interface double layer is formed. This interface electrostatic phenomenon can be observed frequently in everyday life, such as oils transported in pipelines or tankers [4,5] and water flows in porous media [6], as well as in the studies of crystal growth [7], bioengineering [8–10], solar cells [11], absorption and adsorption [12], polymer rheology [13], etc.

As the electrified liquid flows across the solid surface, the steady-state in the double layer can be shifted, leading to a variation in charge density. More importantly, the excess surface charges can be carried away by the liquid, somewhat similar to the mechanism of a water drop electrostatic generator [14] and the well known Milliken's oil drop experiment of electron charge measurement [15]. During this process, a certain amount of mechanical energy is converted to electric energy, which, theoretically, can be employed for mechanoelectric energy conversion for harvesting energy from mechanical motions such as ambient vibrations.

A major hurdle that must be overcome before this technique can be widely applied is the relatively low energy conversion efficiency. Currently, most of the conventional electrostatic generators are suitable only to education or demonstration purposes. The rates of charge separation are still far from being satisfactory. One way to solve this problem is to use nanoporous materials of specific surface areas orders of magnitude higher than that of bulk materials. In a nanoporous material, as the nanopore walls are exposed to the liquid and the charge separation takes place over the large surface area simultaneously, the solid–liquid interface electrostatic effect can be greatly amplified, resulting in an improved mechanoelectric energy conversion efficiency. Recently, a few studies have been carried out in this area [16,17], providing encouraging proof-of-concept results. However, they were mainly focused on the mechanoelectric phenomena in ceramic nanochannels, in the framework of "streaming current". The studies on more electroconductive materials, such as metals and alloys, are scarce. On the one hand, the double layer formation is somewhat independent of the solid conductivity and can be observed at metal–liquid interfaces. On the other hand, a metallic solid can be easily "shorted" so that no voltage can be build up along the solid surface. In the current study, we investigate the liquid electrification in a nanoporous monel electrode. The testing data show that, as the system is

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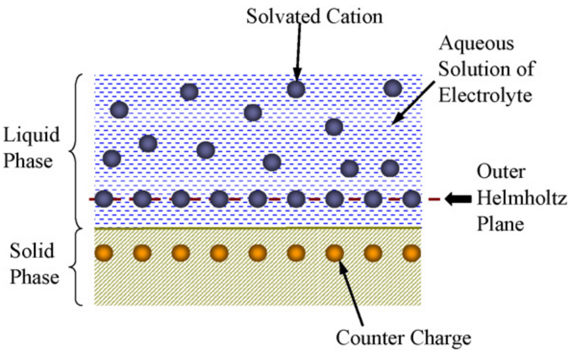

Fig. 1. A schematic diagram of the double layer structure of an electrified solid–liquid interface.

appropriately connected, a significant mechanoelectric potential difference can be measured.

2. Experimental

Fig. 2 depicts the experimental setup. A nanoporous nickel–copper alloy (monel) electrode, with the average pore size of 480 nm, the diameter of 9.5 mm, and the length of 19.0 mm, was tightly inserted in a copper cylinder. The nanoporous electrode was produced through sub-critical sintering of monel nanoparticles at The Chand Eisenmann Metallurgical, Inc., Burlington, Connecticut, USA. The copper cylinder was connected to two polymethyl methacrylate (PMMA) cells, forming a pipeline. The lengths of the copper cylinder and the PMMA cells were 50 and 70 mm, respectively. A 10 wt.% aqueous solution of calcium chloride ($CaCl_2$) was added in the pipeline, supported by the stainless steel piston, with the nanoporous electrode being entirely immersed. The piston was sealed using a reinforced gasket and grounded. A copper counter-electrode ("A") was immersed in the $CaCl_2$ solution, about 5 mm above the nanoporous electrode, and was connected with the copper cylinder by a National Instruments 6936E data acquisition card, so that the potential difference between the two electrodes could be measured continuously. The copper cylinder was connected to the anode and the copper counter-electrode was connected to the cathode.

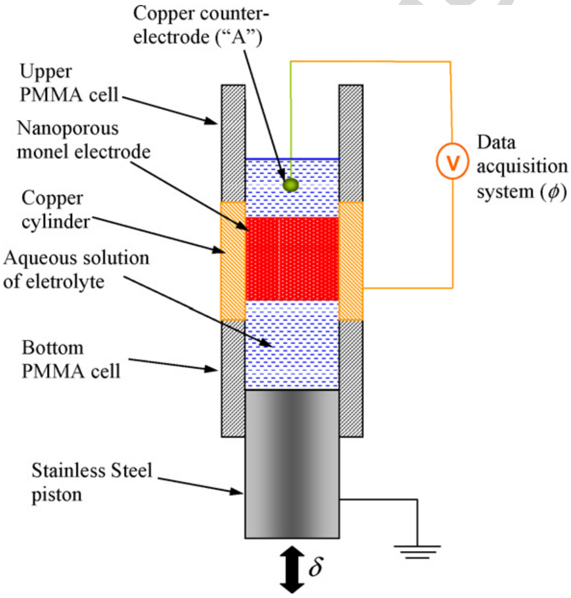

Fig. 2. A schematic diagram of the experimental setup.

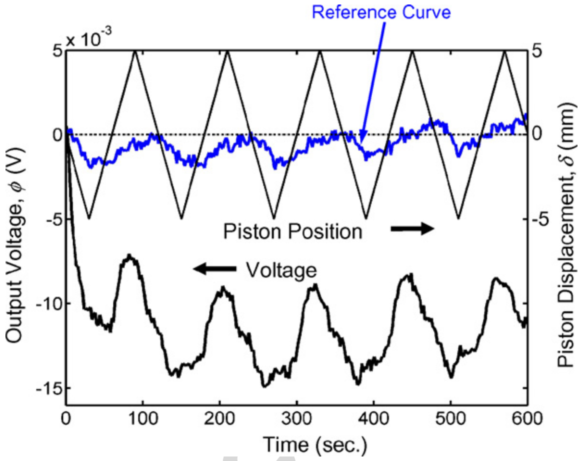

Fig. 3. The relationship between the output voltage, ϕ, and the piston displacement, δ. The black curve is for the nanoporous system, and the blue curve is for the reference system without the nanoporous electrode.

The piston was cyclically moved up and down by ±5 mm at a constant speed of 10 mm min^{-1} using a type 5569 Instron machine. Thus, the $CaCl_2$ solution was driven back and forth through the nanoporous monel electrode. The output voltage was recorded by a Dell Latitude D600 computer, as shown in Fig. 3, where the downward piston displacement is defined as the positive direction. For comparison purpose, a reference curve was obtained by performing the mechanoelectric experiment on a similar system, except that the nanoporous electrode was removed.

3. Results and discussion

Initially, as the piston is at rest, no output voltage can be detected, as it should be, since the copper cylinder, the nanoporous monel electrode, the calcium chloride solution, and the copper counter-electrode form a closed loop with the data acquisition system. The noise is at the level of ±0.5 mV, close to the resolution of the data acquisition board. When the piston is driven by the Instron machine, through Fig. 3, it can be seen clearly that an output voltage is generated, indicating that mechanical work done by the external loading is converted to electricity. The voltage is negative; that is, the potential of the copper cylinder is higher than that of the copper counter-electrode, which should be attributed to that, as the calcium chloride solution flows across the nanoporous electrode, the mobility of the solvated cations in the solid–liquid interface double layer is lower than in the thermal disarray. Due to the absence of confining anisotropic forces from the solid surface, in the interior the solvated cations and the excess unsolvated aions are quite mobile. Consequently, more aions are carried by the liquid phase from the bottom PMMA cell to the upper PMMA cell, i.e.

the liquid phase flowing across the nanoporous electrode tends to be negatively charged. The excess negative charges are collected by the copper counter-electrode, resulting in the measured output voltage. As the flow continues, the excess aions are accumulated and the potential difference between the nanoporous electrode and the counter-electrode becomes increasingly high.

In an ideal case, the liquid electrification is independent of the flow direction. That is, no matter whether the liquid flows from the bottom to the top or from the top to the bottom, the mechanoelectric energy conversion characteristics should be the same. However, since the experimental setup in the current study is asymmetric, fluctuations in potential difference associated with the cyclic piston motion is observed. As the piston reaches the highest position and begins to move downward, the liquid flows back from the upper PMMA cell to the bottom PMMA cell due to the gravity force. Similar charge separation process takes place at the monel–liquid interface in the nanopores but cannot be captured by the data acquisition system, because the piston is grounded. Moreover, as the excess aions move away from the copper couter-electrode, the measured potential difference keeps decreasing, until the piston stops and begins to move upward again. Then, the similar ion separation and accumulation procedure is repeated and the output voltage increases back to the initial level. As a result, as the piston moves back and forth, there is an in-phase output voltage variation.

When the nanoporous electrode is removed from the system, as shown by the reference curve in Fig. 3, the output voltage is negligible, indicating that the experimental observations discussed above is indeed caused by the liquid electrification in the nanopores. The relatively weak output voltage signals of the reference system may be caused by the charge separation at the interface of the liquid phase and the copper cylinder, or, more likely, by the electrostatics associated with the friction in the gasket. Since it is much smaller than the voltage generated in the nanoporous electrode, it can be regarded as a bias error of the testing system. Note that the reference signal is not in-phase with the piston motion. There is an about 60° phase lag between the peaks of the piston position and the reference curve, probably caused by the relatively slow diffusion rate of excess ions in the liquid phase, which becomes pronounced as the distance between the copper counter-electrode and the gasket is relatively large.

Compared with the liquid electrification in nanoporous silica [16,17], the potential difference in the nanoporous monel is somewhat lower but at the same level, suggesting that the mechanoelectric properties are insensitive to the solid conductivity. With the double layer effect being amplified by the large surface area of the nanoporous electrode, this system has great potential in developing advanced energy conversion devices, nanometer to micrometer scale power supply systems, as well as high-sensitivity mechanical motion sensors such as acoustic detectors.

4. Concluding remarks

Through a mechanoelectric measurement experiment, it is validated that nanoporous monel can be used for mechanical-to-electric energy conversion. With the formation of solid–liquid interface double layers in nanopores, the solvated cations are subjected to anisotropic forces and therefore the liquid phase can be electrified spontaneously as it flows across the nanoporous electrode. Since the charge separation occurs simultaneously over the large nanopore surface, a significant potential difference can be measured. The output voltage fluctuation is in-phase with the piston motion. As the nanoporous electrode is removed, the output signal becomes negligible. This phenomenon has great potential in receiving wide applications for energy harvesting, nanometer scale power supply, motion sensing, among others.

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