Int. J. Electrochem. Sci., 7 **(2012)** 2577 - 2583

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Anion Size Effect on Electrode Potential in a Nanoporous Carbon

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Received: 26 January 2012 / *Accepted:* 16 February 2012 / *Published:* 1 March 2012

When two half-supercapacitors are of different temperatures and connected together, since the electrode potential is thermally dependent, a significant output voltage is generated. This thermally induced capacitive effect can be employed for harvesting and storing low-grade heat. In the current study, the effects of anion size are investigated experimentally. In the nanoporous carbon under investigation, the electrode potential increases with temperature. The thermal sensitivity of electrode potential increases somewhat linearly with the anion size, suggesting that using large anions is beneficial. These unique phenomena should be attributed to the unique solvated structures and ion distribution characteristics in the confining nanoenvironment.

Keywords: Electrode potential, Nanporous Carbon, F^-, Cl^-, Br^-, I^-

1. INTRODUCTION

While it has been well known that low-grade heat (LGH) is ample, currently there is still no satisfactory technique that can efficiently harvest and store it [e.g. 1]. By definition, the temperature of LGH is usually lower than 250 ^{o}C. Important LGH sources include the coolants in coal and nuclear power plants, solar thermal energy, geothermal energy, ocean thermal energy, wasted heat in vehicle engines, among others. Due to the low energy density, ordinary thermally triggered phase transformations and chemical reactions are inefficient for LGH storage [2]. Moreover, directly storing thermal energy imposes tough challenges to thermal insulation and energy transportation, and is inconvenient to utilize the energy in other forms.

The major technical difficulties associated with converting LGH to electricity are caused by the relatively low temperature, T. The Carnot cycle efficient is $\zeta_c = \Delta T/T$, with $\Delta T = T - T_r$ and T_r being the reference temperature. For LGH with T in the range of 80 ^{o}C to 200 ^{o}C, ζ_c is only 20% – 40%. Thus, the system efficiency, ζ_c, must be very high so that the overall energetic efficiency ($\zeta = \zeta_c \cdot \zeta_s$) can be sufficient.

However, both direct energy conversion of thermoelectric materials and indirect energy conversion of Organic Rankin Cycle (ORC) engines do not work for LGH as efficiently as for higher temperatures [3], resulting in high power costs around a few to tens of dollars per Watt [4]. The indirect energy conversion methods also demand sophisticated supporting components such as pumps, heat exchangers, etc. that have a large number of moving parts, further much increasing the installation, maintenance, and operational costs [5].

Recently, in an experimental study on nanoporous materials [6], we demonstrated that, except for the classic Seebeck effect, other thermally and electrically related processes can be employed for direct energy conversion, e.g. the thermally affected capacitive effect that will be investigated in the current research. As an electrode is in contact with an electrolyte solution, its surface would be spontaneously electrified as a certain amount of ions are adsorbed [7]. The surface ion layer is formed by the anisotropic force fields from the solid phase and from the liquid phase, characterized by the adsorption coverage (θ). Since the inner Helmholtz plane (IHP) can often be regarded as a monolayer of solvated ions, the surface charge tends to be linear to the adsorption coverage: $Q_e = \alpha \cdot \theta$, where α is a coefficient dependent on the ion and electrode properties. The double-layer structure of surface charges leads to an electrode potential (ϕ) normal to the solid-liquid interface. When temperature rises, due to the variation in ion mobility, the adsorption coverage becomes different, and the surface charge and the electrode potential would also change. As the electric field varies, a certain amount of electric energy is effectively stored in the system. When this capacitive effect is greatly amplified by the large surface area of a nanoporous electrode, the energy density can be very high. Such a system, in essence, becomes a thermally chargeable supercapacitor (TCS), which works in the temperature range of LGH (the working temperature is limited by the boiling point of the electrolyte solution).

The TCS performance is dependent on a large number of system parameters, such as the surface area and properties of electrode materials, the grounding structure, the working temperature range, as well as the liquid phase. In this paper, we will analyze the anion effects.

2. EXPERIMENTAL

The experimental setup is depicted in Fig.1. In two polypropylene (PP) containers, two identical electrodes were immersed separately. The electrodes were made of Cabot BP2000 nanoporous carbon (NC) powders. The NC sample was first refluxed with aceton in a vertical apparatus consisted of a round-bottom flask and an Allihn condenser. The temperature was maintained at 80 ^{o}C by a thermal mantle for 4 h, followed by drying in a VWR 1410 vacuum oven at 80 ^{o}C for 12 h. Then, about 200 mg of NC powders were compressed in a stainless steel mold by a type 5580 Instron machine at 400 MPa for 5 min, forming an electrode disk. By using a Micrometritics TriStar-

3000 Gas Absorption Analyzer, a Brunauer-Emmett-Teller (BET) analysis was performed and the specific surface area was measured as 1810 m^2/g. The nanopore size had a relatively broad distribution from the mesoporous range (2 nm) to the macroporous range (~100 nm), with the modal value at about 3 nm. Each electrode contained a NC disk and a platinum (Pt) foil charge collector that were firmly compressed together.

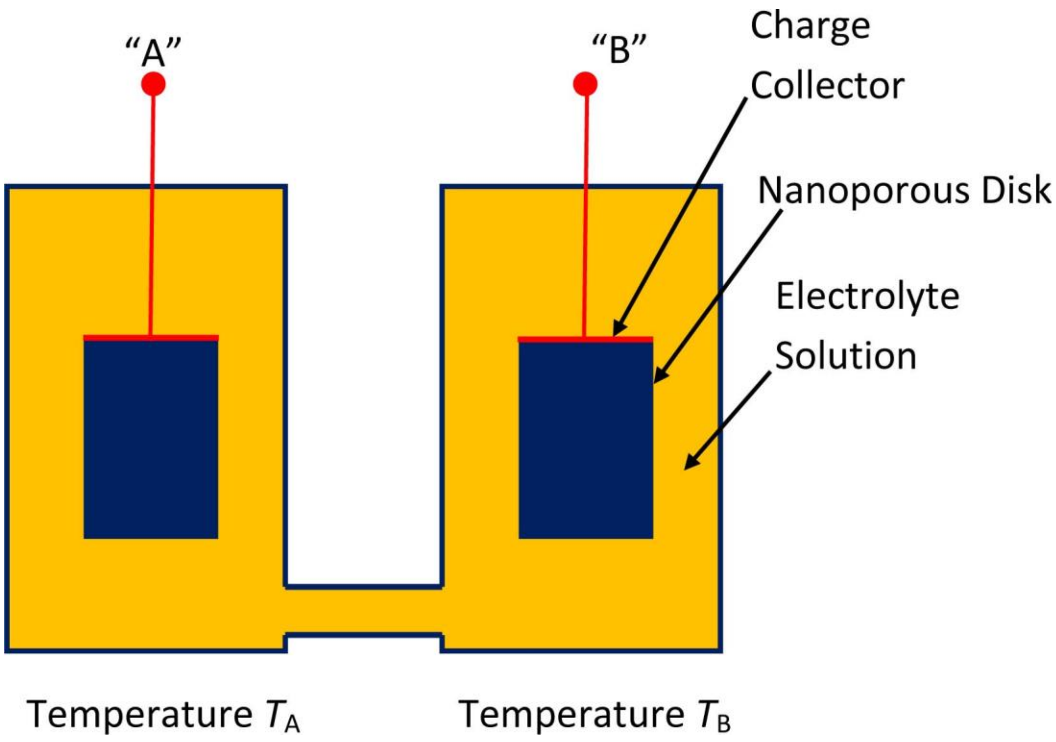

Figure 1. Schematic of a TCS.

The surface area of each Pt foil was 1 cm^2. The electrodes were soaked in an electrolyte solution. The potential difference between the two electrodes (V) were measured between "A" and "B" by a National Instrument SCB-68 Data Acquisition (DAQ) system. The components were connected by Pt wires. The circuit was completed by a salt bridge between the two containers. The diameter and the length of the salt bridge were 5 mm and 30 mm, respectively.

By using a Corning PC-220 hot plate, the liquid in one of the containers was heated, with a constant heating rate of 3 ^{o}C/min. The other container was kept at 21 ^{o}C by using a cold water bath. The liquid phase was a 1 M aqueous solution of sodium salt. The solute was either sodium fluoride (NaF), sodium chloride (NaCl), sodium bromide (NaBr) or sodium iodide (NaI). Figure 2 shows the typical output voltage, through which the average temperature sensitivity of output voltage (dV/dT) can be calculated, as shown in Fig.3.

Reference experiments were carried out on the charge collectors. The setup was similar with the NC system, except that the two NC disks were removed. The testing results of V and dV/dT are also shown in Figs.2 and 3.

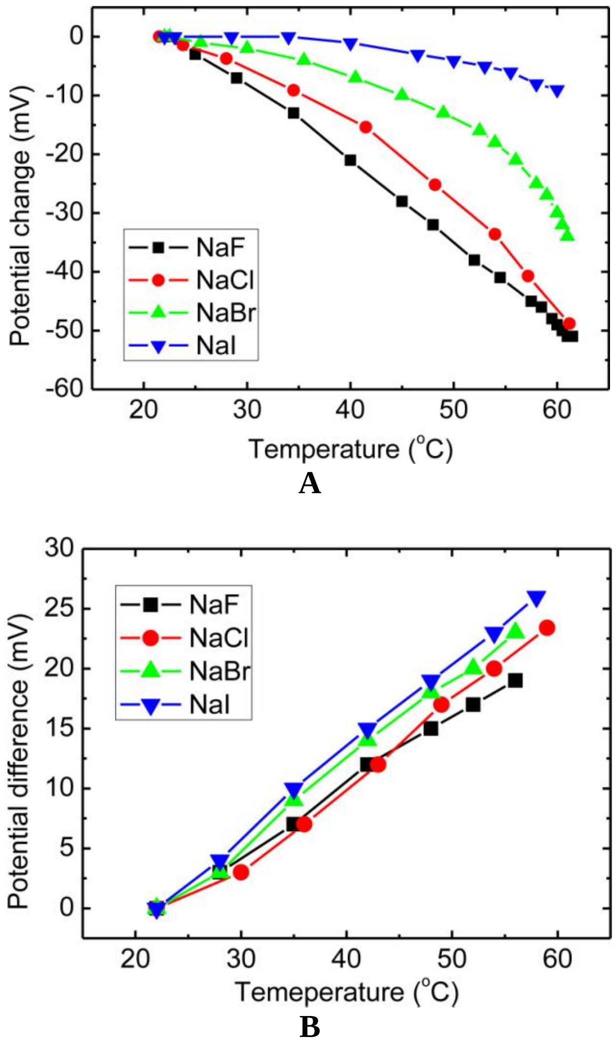

Figure 2. Typical results of the output voltage (*V*): (a) the reference system; and (b) the nanoporous carbon system. The ion concentration is 1 M.

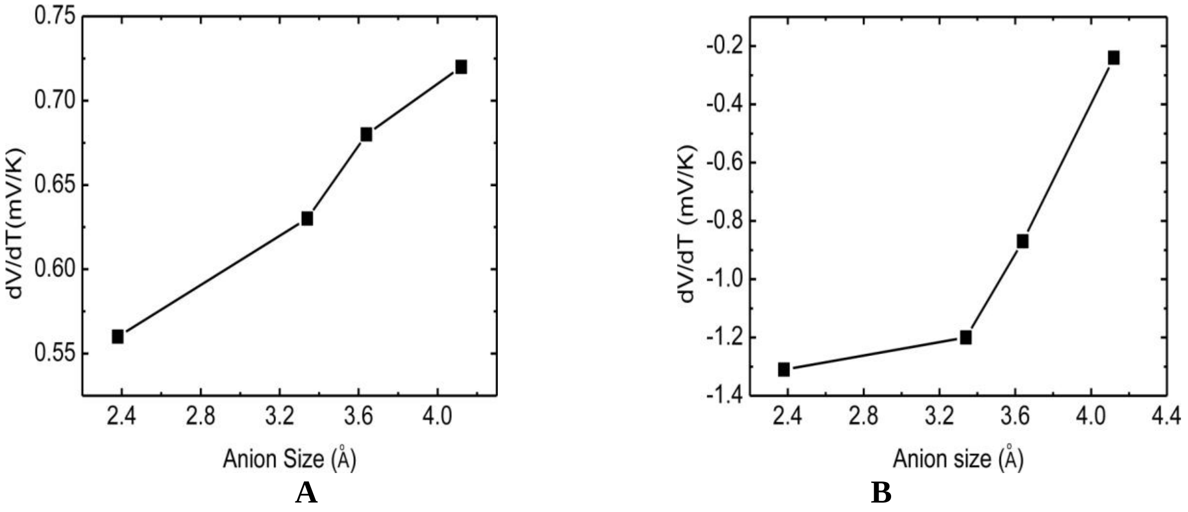

Figure 3. The temperature sensitivity of electrode potential (|d*V*/d*T*|) as a function of the anion size: (a) the nanoporous carbon system; and (b) the reference system.

3. RESULTS AND DISCUSSION

All the tested samples are of the same electrode materials, solution (water), ion concentration (1 M), cation (Na^+), and anion charge. The only difference among them is the anion specie, particular the anion size (D). According to literature data, the anion sizes for F^-, Cl^-, Br^-, and I^- are 0.238 nm, 0.334 nm, 0.364 nm, and 0.412 nm, respectively.

In the reference system, the electrode is the Pt foil. Initially, when the temperatures of both containers are the same, the output voltage is zero, since both sides have the same electrode potential. As the temperature of one container (T) increases, its electrode potential is reduced, suggesting that the surface density of anions becomes lower. According to the classic Temkin isotherm [8], $\theta = (k_B T/B)\ln[W\cdot C\cdot\exp(Q_o/K_B T)]$, where k_B is Boltzmann constant, W and B are system parameters related to the molecular and ion distribution, and Q_o is the heat of adsorption. The electrode potential can be derived as: $\phi = (1/K_e+1/K_{IHP})\beta\theta$, where K_e and K_{IHP} are the integral capacitances of from electrode to IHP and from IHP to bulk solution, respectively; β is a system parameter dependent on the interaction among solid atoms, solvent molecules, and solvated ions. Since the reference temperature (T_r) is constant, $\mathrm{d}V/\mathrm{d}T = \mathrm{d}\phi/\mathrm{d}T$. Thus,

$$\frac{\mathrm{d}V}{\mathrm{d}T} = -\frac{1}{K_{\mathrm{IHP}}}\left[\frac{k_B}{B}\ln(W\cdot c)+\frac{1}{B}\frac{\mathrm{d}Q_0}{\mathrm{d}T}\right] \tag{1}$$

with c being the ion concentration. The measurement data of the reference experiment show that the temperature sensitivity of the output voltage of the Pt foil increases as the anions are smaller. That is, the adsorption of smaller anions is more sensitive to the temperature change. According to Eq. (1), the temperature dependence of the heat of adsorption ($\mathrm{d}Q_0/\mathrm{d}T$), which is related to the ionic size and shape [9], affects $\mathrm{d}V/\mathrm{d}T$. In essence, $\mathrm{d}Q_0/\mathrm{d}T$ reflects the change in heat capacity (ΔC) before and after ion adsorption [10]. In a bulk liquid phase, an anion is solvated by a few water molecules. When it approaches an electrode surface, it may lose a portion of the hydration shell, so that the heat capacity varies. Because a smaller anion has a higher hydration number [11], $\mathrm{d}Q_0/\mathrm{d}T$ of smaller anions tends to be higher, so is $\mathrm{d}V/\mathrm{d}T$.

As NC disks are employed in the system, due to their large capacitance associated with the ultrahigh surface area (10^6 times larger than the surface area of Pt foil), they would dominate the output voltage (V). It can be seen from Fig.2 that $\mathrm{d}V/\mathrm{d}T$ becomes positive; that is, the effective electrode potential increases with temperature, which is contradictory to the prediction of the classic theory discussed above. This unique phenomenon may be associated with the confinement effect of nanopore walls. Usually, nanoporous carbons have acidic surface functional groups, such as hydroxyl or carboxylic groups. These negatively charged groups suppress the infiltration of anions [10], and a temperature variation mainly affects the configuration of cations. The desorbed ions must diffuse along the axial direction of the nanopore to reach the ion reservoir outside, which has different characteristic time scales from the electrode potential change. As temperature increases, both the adsorption coverage and the diffusion characteristics would vary. If the latter changes faster than the former, even when the effective θ decreases, the overall electrode potential may still increase.

Another interesting phenomenon is, when the anion size increases, the electrode potential becomes more thermally sensitive, and d*V*/d*T* increases. For the smallest anion of F^-, d*V*/d*T* is around 0.53 mV/°C; as the anion size becomes larger (Cl^-), d*V*/d*T* increases to nearly 0.63 mV/°C; when the anions are the even larger Br^- and the largest I^-, d*V*/d*T* are ~0.67 mV/°C and ~0.72 mV/°C, respectively. The d*V*/d*T*-*D* relationship is somewhat linear. From the testing data shown in Fig.3(a), there is no clear evidence showing that whether the anion size effect is more pronounced when *D* is relatively small or large. This result cannot be explained by the classic theory that the system free energy associated with ion adsorption is smaller for larger anions [16] – As the IHP of larger anions tends to be more stable, its thermal sensitivity should be lower.

In a nanopore, the solid phase may cause a “squeezing” effect [17]. The combined influences from both the cations and the anions can lead to the opposite trend in d*V*/d*T* change. Particularly, as the solvated structures of larger anions are less stable, stronger bonds would be formed with the solvated cations and/or water molecules. Such a larger-scale structure can be more sensitive to the temperature change, so that the variations in the adsorption coverage and the electrode potential are promoted. Another possible mechanism, similar with the above discussion on the ϕ-*T* relationship, is related to the confined ion diffusion in nanopores. As the hydration shells of larger anions are relatively unstable, their thermally driven diffusion can be easier than that of smaller ones. Thus, the confined structures of smaller anions are farther away from the equilibrium, resulting in the reduced thermal sensitivity of effective electrode potential.

4. CONCLUDING REMARKS

To summarize, through an experimental study on a nanoporous carbon based TCS, it is found that anion size has significant effects on the thermal sensitivity of electrode potential. Contradictory to the prediction of classic theories, the electrode potential increases with temperature, which may be attributed to the lack of bulk phase in nanopores. Moreover, |d*V*/d*T*| increases with the anion size; that is, with everything else being the same, increasing anion size has a beneficial effect. Qualitative discussions are given for these unique phenomena. The detailed mechanisms and processes are still under investigation.

ACKNOWLEDGEMENTS
The concept development was supported by the State of California EISG Program under Grant No. EISG-08-13. The materials processing was supported by the National Science Foundation under Grant No. ECCS-1028010. The materials characterization was supported by the National Science Foundation under Grant No. IIP-1045681.

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