Characterization of electrical conductivity in a zeolitelike material

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We present the electrical characterization of a zeolitelike oxo-vanadium arsenate framework. The experimentally obtained electronic and ionic conductivities and their interactions are discussed. Further, we investigate the potential use of electrically conducting zeolitelike materials in electrical energy storage applications, in light of the material's structural and electronic characteristics. © *2009 American Institute of Physics.* [doi:10.1063/1.3251070]

Development of different directions to improve electrical energy storage capabilities is essential to meet the current and future requirements for efficient use of electrical energy in applications. Materials are needed to improve charge storage capabilities by increasing both the energy and the power densities, as well as achieving faster recharge times. In this letter, we present an electrically conducting zeolitelike microporous framework, and discuss how this type of material would find applications in electrical double-layer capacitive storage.

The electrical double-layer capacitor (EDLC) forms the basis for ultracapacitors, where the layer is formed between mobile ions in an electrolyte and an electrically conducting plate.[1,2] The capacitance per unit area is high due to the short charge separation distance characteristic of ionic double layers typically atomic in scale. The high attainable capacitance forms the basis for widespread similar electrolytic capacitors. An ultracapacitor adds to this a large effective area of the capacitor plate by employing a porous conducting medium as electrode. The capacitance values correlate with pore dimension and ion size,[3] as well as with pore size distribution.[4]

Zeolitelike materials present high effective area due to the unusually dense and regular network of channels and pores defined by the crystal structure.[5] Pore dimensions in microporous zeolites are influenced by the synthetic conditions, allowing control over the pore size and its distribution. We illustrate how the double-layer concept carries over to a zeolitelike material, as in Fig. 1(a), where we present how a positive charge residing in a zeolite pore may induce a distribution of compensating charges from electrons in the framework. The double-layer separation is, as usual, atomic in scale leading to high capacitance in this geometry. However, for zeolitelike materials to serve as EDLC charge storage units, a framework is needed that supports electronic conductivity. We present such an example with an oxo-vanadium arsenate zeolitelike material, and discuss its potential use for EDLC applications.

The oxo-vanadium arsenate is synthesized through hydrothermal methods. The three-dimensional framework of this material, as obtained by single crystal x-ray diffraction, is depicted in Fig. 1(b), and delineates channels that run down the three crystallographic directions. Extra-framework constituents, here the organic template organoammonium cation, and water (omitted from the figure for clarity), are situated in the channels which intersect along the diagonals of the cube. The framework shown in Fig. 1(b) is generated from idealized coordinates for the framework atoms in the space group $Im\bar{3}m$. The structure exhibits disorder potentially influencing the measured electrical characteristics. Details of the synthesis and single crystal diffraction analysis will be reported elsewhere, and we state that the presence of the organic template is crucial for the isolation of this particular material. The material is microporous, with accessible pore dimension of 0.5 nm. The extra-framework constituents within the pores of the as-synthesized material may be removed by heating under an inert atmosphere or through intercalation reactions. Thermogravimetric analysis indicates the temperatures at which the extra-framework constituents are expelled, recorded as a loss in weight of the sample. Weight loss starts around 340 K, and by 370 K a considerable weight loss has occurred, attributed to the loosely held water inside the pores. A second weight loss occurs around 470 K, and a third around 600 K, attributed to tightly held water and the organoammonium template inside the pores, respectively. Above 600 K, the framework pores are void, leaving an empty framework which is stable up to 770 K.

The zeolitelike material reported here exhibits mixed conductivity: ionic due to the extra-framework constituents, and electronic due to the framework. We investigate the contributions and interplay of the parallel ionic and electronic conduction pathways through measurement of the electrical conductivity (σ) as a function of temperature (T). Conductivity values are obtained from electrical resistance measurements on single crystals contacted with silver epoxy.[6] The measured room temperature conductivity of a cube with
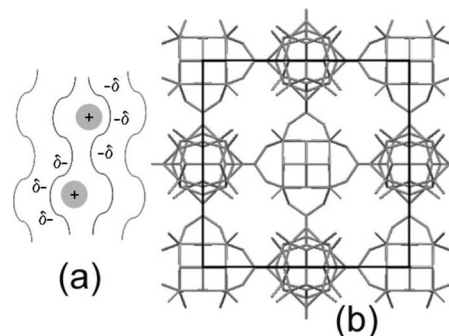

FIG. 1. (a) Schematic diagram of a positive charge in a pore defined by the zeolitelike framework, and the distribution of induced counter charges (δ) in the framework. (b) Stick representation of the framework down the *a* axis with cell edges of 1.66 nm delineated in black. Extra-framework constituents omitted for clarity. The accessible dimension of the pore is 0.5 nm.
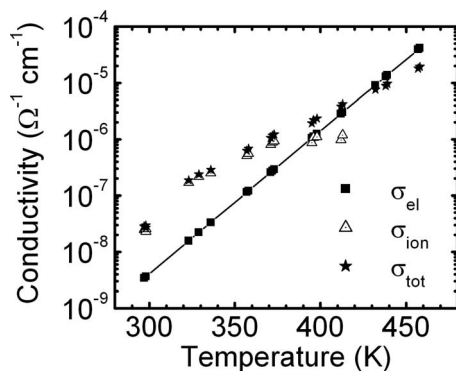
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FIG. 2. T dependence of the total conductivity σ_{tot} ($\star$), electronic conductivity σ_{el} ($\blacksquare$), and ionic conductivity σ_{ion} ($\triangle$), in a semilog plot. Measured are σ_{tot} and σ_{el}, while σ_{ion} is obtained by the difference between σ_{tot} and σ_{el}. An exponential T dependence of σ_{el} is observed.

FIG. 3. T dependence of σ_{ion}, plotted as $T^{3/2}\sigma_{ion}$ vs $1/T$, as the best fit to the data for 290 K $\leq T \leq$ 380 K. The slope yields an activation energy for hopping of ions within the pores and channels of the framework, here with a value of 0.50 eV.

~ 50 μm edge is $\sigma = 3.3 \times 10^{-8}$ Ω^{-1} cm^{-1}. The contribution of the ionic conductivity (σ_{ion}) may be obtained by subtracting the electronic conductivity (σ_{el}) due to the empty framework from the total conductivity (σ_{tot}), as seen in Fig. 2, since both the parallel electronic and ionic conductivities contribute to σ_{tot}, attributable respectively to the framework and the extra-framework constituents (here water plus organoammonium ions). In Fig. 2 we plot the various σ, as $\log(\sigma)$ versus T. Initially, σ_{ion} ($\triangle$) increases as T increases, but, around 380 K, the trend levels off. Indeed, σ_{ion} is influenced by the loss of extra-framework ions resulting in a decrease in protonic conduction and a hydration-dependent change in ion mobility.[7,8] Deriving reliable values of σ_{ion} above 380 K is further influenced by the fact that at higher T, σ_{el} ($\blacksquare$) eventually dominates σ_{tot} ($\star$). Reliable measurements of σ_{ion} extend to 420 K only, although σ_{ion} is obtained up to 465 K. In short, for $T > 380$ K, the measured σ_{tot} is dominated by the electronic contribution, while at low T, σ_{tot} is dominated by the ionic contribution. The decrease in water and organoammonium ions at the higher T influences σ_{el}, as σ_{el} then, within the accuracy of the data, increases above the value obtained for the full framework. Hence, both conduction mechanisms are interdependent, as expected if the presence of extra-framework ions leads to more localized electronic states, reducing the mobility. Below we investigate σ_{el} in additional detail.

To access electronic transport, measurements were performed on the empty framework, namely material where the extra-framework constituents are expelled from the pores under a thermal treatment. As mentioned above, when the material is heated up to 600 K, the extra-framework constituents, here water plus organoammonium, are expelled yielding an empty framework. The framework is backfilled with N$_2$ and kept under an overpressure of N$_2$ to avoid reoccupation of the channels with water for subsequent measurements. The variation in σ_{el} as a function of T for the oxovanadium arsenate empty framework is depicted in Fig. 2 by the $\blacksquare$ and solid line. We observe σ_{el} increasing exponentially with increasing T, indicative of nonmetallic conduction. The T dependence does not follow standard expressions for one-dimensional, two-dimensional or three-dimensional Mott variable range hopping,[9,10] or for activation across an energy gap, excluding these known mechanisms of electron transport even when accounting for the effective dimensionality (one, two, or three) of electron dynamics in the framework.
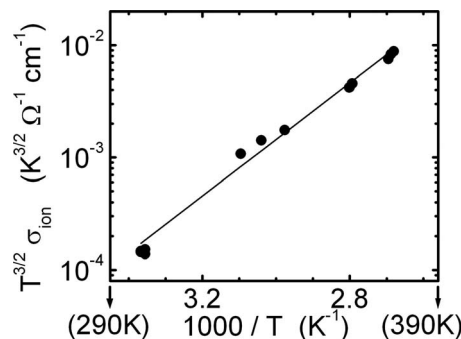
Electronic conductivity in the material is likely influenced by coupling to the ionic degrees of motion, with polaronlike contribution.[11,12] However, a detailed model must await further experiments on this class of materials.

Next, we investigate the ionic contribution, defined as $\sigma_{ion} = \sigma_{tot} - \sigma_{el}$. Figure 3 depicts the T dependence of σ_{ion}, and we plot the data up to 420 K. Above 380 K, σ_{ion} saturates to a near constant value as discussed in relation to Fig. 2, as extra-framework constituents (water plus organoammonium) are expelled from the framework. Here we focus our discussion of the dependence on T to $T \leq 375$ K. A simple Arrhenius-activated model of ionic transport[7,8,13] does not fit well. A better fit is obtained if we consider channeling of ions through a sublattice of attachment sites in the framework, through a mechanism that at least includes phonon-assisted hopping.[11,14] Theoretically, σ_{ion} then obeys $T^{3/2}\sigma_{ion} \propto \exp(-E_A/k_B T)$, where E_A denotes a characteristic activation energy required for ion hopping from attachment site to attachment site.[11,14] This relation is borne out experimentally with $E_A \approx 0.50$ eV, and indeed physically leads to an acceptable picture of ion conduction in zeolitelike materials, where channels and attachment sites can be identified within the framework.

The oxo-vanadium framework is robust toward intercalation. The organoammonium cation may be exchanged with inorganic cations, and e.g., the K$^+$ exchanged framework exhibits no change in its crystalline framework as determined by single crystal x-ray diffraction. The robustness of the framework, coupled with the electronic characteristics observed, yield a good candidate for EDLC applications. In a capacitor, the stored energy U is expressed by $U = \frac{1}{2}CV^2 = \frac{1}{2}QV$, where C is the capacitance, Q the stored charge, and V the voltage. A high Q per material volume is an advantage, realized by the high pore density in a zeolitelike material. Equivalently, U increases when C increases, and a high C is realized in zeolitelike EDLCs by the electrical double-layer storage and high effective area.[2] Thus an electrically conducting zeolitelike material would allow for a substantial increase in U over presently available materials.

In Fig. 4 we present a schematic concept of an EDLC with two conducting oxo-vanadium arsenate frameworks attached to an external voltage source. An ion membrane is located in between, permeable to the electrolyte ions. One framework is positively charged and hosts negative ions inside its structure, the other vice versa. In series, they form a storage capacitor $\frac{1}{2}C$. We note that charging and discharging
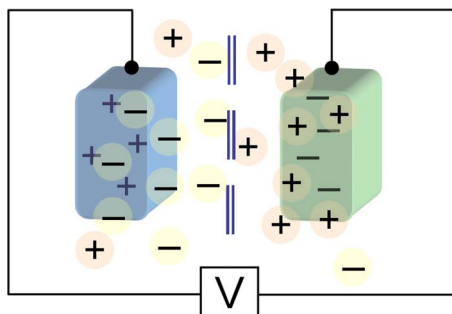
FIG. 4. (Color online) Concept of zeolitelike frameworks used in EDLCs. Two frameworks are connected to an external voltage source, with an ion permeable membrane located in between. Electrolyte ions are represented as spheres.

in principle does not consume material, promising the many charge-discharge cycles inherent in the capacitor concept. Preliminary calculations of energy stored in our oxo-vanadium arsenate structure indicate a factor of 5–8 increase in Q and C per material volume over mesoporous carbon.[15,16] Indeed, the effective area per unit volume of material, α, is approximated by $\alpha = 6p/D$ where p denotes the fraction of pore volume to total material volume and D denotes the average pore diameter. In the microporous oxo-vanadium arsenate with a pore diameter of 0.5 nm, p is higher and D is smaller than in mesoporous carbon, resulting in a substantial increase in C and Q. Preliminary capacitance measurements validate the calculated ~8-fold increase. Further measurements are on going, to more fully characterize the electronic and ionic conductivities and their interplay, and the double-layer properties in the oxo-vanadium arsenate

material. In summary, electrically conducting zeolitelike frameworks offer promising avenues in electrical energy storage, with ultracapacitors as specific examples. Yet, uses for electrically conducting zeolitelike frameworks can be envisioned in other important energy applications, e.g., in ion-exchange membrane technologies and catalysis.

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