

Charge Insertion and Transport at Mesoporous Nanoarchitectures of V_2O_5 and MnO_2

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Recent investigations of charge-insertion behavior of sol–gel-derived nanoscale, mesoporous, networked charge-insertion oxides, particularly vanadium hydrous oxide in which the Li-to-V ratio is ~ 2 and not limited to 0.5 as in polycrystalline V_2O_5 [1,2], has revealed that these nanoarchitectures store charge in three ways, via: (1) double-layer capacitance; (2) energy-specific insertion of cations (as seen in standard intercalation battery materials); and (3) pseudocapitance. Materials that blend all three mechanisms of charge storage function as inherently hybrid power sources that can deliver both high peak power and sustained low power. The ability to store both battery-like and ultracapacitor-like charge is attributed to the adjustable disorder present in these nanomaterials [3-5].

Characterization of these architectures first as nanomaterials, secondly as charge-storage materials, and finally with respect to how charge is transported on the nanoscale in these pore–solid architectures requires an array of physical, structural, chemical, and electrochemical approaches. Because charge-insertion reactions are intrinsically electrochromic, spectroelectrochemical studies provide an independent measure of the electronic state of the transition metal during cation insertion as a function of the particular metal oxide, its defect character, and the nature of the pore–solid architecture [5,6].

The nature of the pore–solid nanoarchitecture of aerogels (derived from wet gels dried with essentially no pore collapse) and ambigels (derived from wet gels processed from nonpolar, low surface tension pore fluids with retention of the mesoporous network) imparts new aspects to charge transport on the nanoscale. The innate pore–solid architecture of aerogels and ambigels melds high surface area expressed as a dendritic, self-wired, covalently bonded network of oxide domains with a continuous, mesoporous network for rapid diffusional flux of reactants and products. In rate-critical applications (sensing, energy-storage, energy–conversion, synthesis), multifunctional materials expressed as ambigels or aerogels respond 10–1000 times faster than do nanostructures with 2-D or 3-D porosity [3,7].

The continuity of the mesoporous network is a critical component in establishing the high-rate character of these architectures. Conductimetric

studies with ambigel birnessite MnO_2 has led to the discovery of another property of continuous porosity: the existence of proton wires that are sustained only in monolithic nanoarchitectures of the oxide and yield $>10\times$ higher sensitivity to humidity over nanoparticulate films of the oxide [8].

The typical nanocrystalline, mixed-conducting oxides of interest in electrical and electrochemical applications are used as non-bonded nanoparticles that amplify grain-boundary contributions and create large charge-transfer resistances that can limit performance. The continuous, covalently linked solid network in aerogels eliminates these boundaries, necessitating a fundamental study into the conductive behavior of such continuously linked networked nanowires.

The continuity of the nanoscopic pore and solid networks over macroscopic dimensions (micrometers to centimeters) establishes a 3-D transport connectivity difficult to achieve with other nanostructured charge-insertion materials. Such nanoarchitectures challenge the standard ways in which electrochemically active oxides are understood and used for energy storage.

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