Research paper

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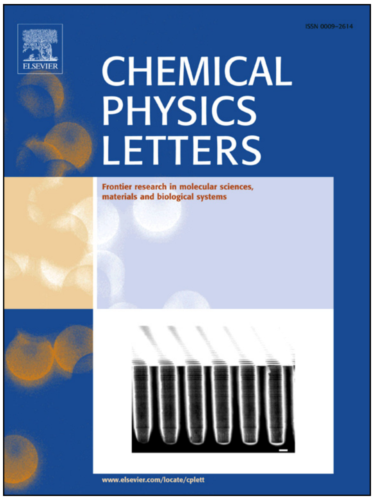

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In-pore exchange and diffusion of carbonate solvent mixtures in nanoporous carbon

Todd M. Alam[a,*], Thomas M. Osborn Popp[a,b]

[a] *Department of Organic Materials Science, Sandia National Laboratories, Albuquerque, NM 87185, USA*
[b] *Department of Chemistry, University of California Berkeley, Berkeley, CA 94720, USA*

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ABSTRACT

High resolution magic angle spinning (HRMAS) ^{1}H NMR spectroscopy has been used to resolve different surface and in-pore solvent environments of ethylene carbonate (EC) and dimethyl carbonate (DMC) mixtures absorbed within nanoporous carbon (NPC). Two dimensional (2D) ^{1}H HRMAS NMR exchange measurements revealed that the inhomogeneous broadened in-pore resonances have pore-to-pore exchange rates on the millisecond timescale. Pulsed-field gradient (PFG) NMR diffusometry revealed the in-pore self-diffusion constants for both EC and DMC were reduced by up to a factor of five with respect to the diffusion in the non-absorbed solvent mixtures.

1. Introduction

Currently there is a growing need for energy storage technologies for application in electric vehicles, mobile electronic devices, and grid energy storage. Electrochemical capacitors, often known as supercapacitors, are a promising energy storage candidate for uses where rapid delivery of high power is required [1-3]. The class of supercapacitors known as electrochemical double layer capacitors (EDLC) use porous, high surface area, carbon electrodes immersed in a liquid electrolyte to achieve charge separation resulting in high capacitance and high power density, but with lower energy density than lithium-ion batteries [4]. To achieve higher energy densities and yet still maintain high power density, lithium-ion capacitors (LIC) have been developed which aim to bridge the gap between batteries and supercapacitors [5-9]. During charging and discharging of an LIC, lithium ions intercalate in and out of a graphite negative electrode, while anions adsorb and desorb to and from the surface of the positive electrode. The positive electrode is usually made from a porous carbon material. Electrolyte solvents for EDLC and LIC commonly involve mixtures of carbonate solvents, including the 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Carbonate solvents readily dissolve lithium ions, operate within a large electrochemical window, form a very stable solid electrolyte interphase (SEI) layer on the graphite negative electrode, and are considered “green” solvents due to their relative non-toxicity and the fact that they can be synthesized using CO_2 as a feedstock [9-11].

Activated carbon (AC) and nanoporous carbon (NPC) materials are ideal electrode materials for symmetric EDLC, and for the positive electrode in asymmetric LICs, due to their high conductivity and surface area [12-15]. These carbon materials are comprised of sp^2-hybridized graphene-like sheets organized in a porous, amorphous structure [16,17]. Ultimately it is the transport and adsorption of ions in NPC that determines the EDLC and LIC power storage and discharge characteristics. The contributions that surface area, surface defects, pore size distributions, pore tortuosity, pore alignment, electrolyte diffusion, and solvent shell rearrangement have on ion transport within carbonaceous materials remains a topic of debate [18-22]. These questions have led to the development of many different NPC systems with specific tailored surface and pore properties [15,19,22-25]. Understanding the interactions between electrolyte molecules and porous carbon electrode materials is critical to improving the design of EDLCs and LICs, in particular the rate of transport of the electrolytes within the electrodes.

Nuclear magnetic resonance (NMR) spectroscopy provides a non-invasive and highly selective method for probing these interactions. Previous NMR studies of electrolytes in porous carbon materials have focused on the adsorption, organization, and degree of infiltration of ions within the pores [20,26-31]. Large changes in the chemical shift of electrolyte molecules occur upon adsorption into a porous carbon material as a result of diamagnetic ring current effects, making it experimentally straightforward to isolate and study populations of molecules

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* Corresponding author. Tel: 1-505-844-1225
E-mail address: tmalam@sandia.gov (T.M. Alam)