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Self-diffusion of electrolyte species in model battery electrodes using Magic Angle Spinning and Pulsed Field Gradient Nuclear Magnetic Resonance

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HIGHLIGHTS

- Diffusion of electrolyte species is measured in model electrodes by MAS-PFG-NMR.
- Carbon black interacts with lithium ions.
- Mesoporosity and surface interactions slow the diffusion of Li^+ or PF_6^-.

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ABSTRACT

Lithium-ion batteries are electrochemical storage devices using the electrochemical activity of the lithium ion in relation to intercalation compounds owing to mass transport phenomena through diffusion. Diffusion of the lithium ion in the electrode pores has been poorly understood due to the lack of experimental techniques for measuring its self-diffusion coefficient in porous media. Magic-Angle Spinning, Pulsed Field Gradient, Stimulated-Echo Nuclear Magnetic Resonance (MAS-PFG-STE NMR) was used here for the first time to measure the self-diffusion coefficients of the electrolyte species in the LP30 battery electrolyte (i.e. a 1 M solution of $LiPF_6$ dissolved in 1:1 Ethylene Carbonate - Dimethyl Carbonate) in model composites. These composite electrodes were made of alumina, carbon black and PVdF-HFP. Alumina's magnetic susceptibility is close to the measured magnetic susceptibility of the LP30 electrolyte thereby limiting undesirable internal field gradients. Interestingly, the self-diffusion coefficient of lithium ions decreases with increasing carbon content. FIB-SEM was used to describe the 3D geometry of the samples. The comparison between the reduction of self-diffusion coefficients as measured by PFG-NMR and as geometrically derived from FIB/SEM tortuosity values highlights the contribution of specific interactions at the material/electrolyte interface on the lithium transport properties.

1. Introduction

Lithium-ion batteries have proven their reliability through their prominence in numerous electronic devices [1]. For vehicle applications, batteries must be able to deliver both power (torque) and energy (mileage). The advent of electric cars and smaller yet power hungry electronic devices demanded greater energy and power densities than were necessary a decade ago. Most studies aim to tackle this problem by introducing better active materials able to cycle efficiently for many cycles and at high C-rates [2–4].

Lithium ion transport is also a deciding factor in battery performance at high rates. Two factors affect this process namely the

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SEI layer [5–8] and the electrode architecture [14,15]. However, industry has shown a particular interest in electrode formulation and architecture. The electrode architecture problem is not new for the battery research community as numerous studies, mostly mathematical, have shown which parameters are key for efficient electrode architectures [9–11]. One of the highlighted goals is to increase the loading and make the electrodes thicker while maintaining decent transport properties, in order to increase the proportion of active materials in the whole battery, thereby increasing energy capacity. However, the increase in electrode thickness also increases the path lengths for charge transport within the electrodes. At high current rates, the performance of the battery is indeed limited through the diffusion of the lithium-ion within the porous network [12–15]. This could be resolved by thoroughly investigating the effects of pore morphology on the diffusion coefficient of the lithium-ion as well as the electrolyte species. Until now, no single experiment managed to successfully measure lithium-ion diffusivity inside the pores of a lithium-ion battery electrode. Traditional electrochemical characterization techniques and microscopy are unable to determine the diffusion coefficients of the electrolyte species in porous media. In the present study, Pulsed Field Gradients (PFG) are used to measure the self-diffusion coefficients of mobile species in stimulated echo (STE) ^{7}Li or ^{19}F Nuclear Magnetic Resonance (NMR) experiment. The anisotropic magnetic interactions, which lead to a strong broadening of the peak observed for electrolyte species are removed with slow Magic Angle Spinning (MAS) to improve the sensitivity of the PFG-STE experiments while avoiding centrifugation of the electrolyte out of the electrode material [16,17].

PFG-STE was developed in the early 1960's, notably as a method for measuring diffusivity of oil in porous rocks to aid oil surveys [18–22]. The attenuation of the stimulated echo signal as a function of the magnetic field gradient strength can be related with the self-diffusion coefficient in the Stejskal-Tanner equation [23–25]:

$$\frac{S(g)}{S(g=0)} = \exp\left[-D\gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3}\right)\right] \tag{1}$$

where D is the self-diffusion coefficient of the species being observed, γ is the gyromagnetic ratio of the spin bearing atom, g is the applied gradient strength, Δ is the diffusion delay and δ is the effective gradient pulse length. Many investigations concerned self-diffusion coefficients of electrolyte species in bulk electrolytes [26,27] and diffusivity within separators and membranes [28–30] or *in situ* in supercapacitors [31]. However, it has never been applied to battery electrodes.

The measurement of self-diffusion coefficients PFG-STE NMR is difficult when diffusion occur within strong internal field gradients generated by discontinuities of the magnetic susceptibility, which lead to fast and non-refocusable decay of the magnetization. Magnetization experiments show that the magnetic susceptibility of LP30 battery electrolyte (i.e. a 1 M solution of $LiPF_6$ dissolved in 1:1 Ethylene Carbonate - Dimethyl Carbonate) is closest to the one measured for alumina. Therefore, the transition metal-based lithium-ion battery electrode materials were replaced with alumina powders with controlled morphologies. The model electrode contains the standard binder and carbon additives. In addition, conductivity measurements and SEM microscopy were also performed on our model electrodes to check their suitability as model electrodes. These results can be found in the supplementary information section.

Focused ion beam (FIB) combined with scanning electron microscopy (SEM) tomography was used for the analysis of 3D geometries of our samples. FIB/SEM was recently applied in lithium-ion batteries to explore relationships between electrode architecture and electrochemical performance [32–38].

2. Experimental

2.1. Magnetic susceptibility of LP30

Polycarbonate capsules were dried in a vacuum oven at 50 °C and filled with LP30, which has the following composition: 1 M $LiPF_6$ dissolved in 1:1 Ethylene Carbonate (EC) - Dimethyl Carbonate solution (DMC) and purchased from Solvionic. The mass of LP30 was measured before inserting the samples in a commercial SQUID magnetometer (Quantum Design, MPMS) to allow proper determination of the mass susceptibility (cm^3 g^{-1}) at room temperature. The applied field varied between 1000 and 10000 Gauss. Data were corrected for the contribution of the sample holder. The magnetic moment of LP30 was determined through the following equation: $M = \chi H$, where M is the magnetization in emu g^{-1}, χ is the magnetic susceptibility in cm^3 g^{-1} and H is the field in Oe (see Supporting Information's section VI).

2.2. Preparation of composites

The following reagents and compounds were used to prepare model slurries, powder mixtures and model systems: Al_2O_3 (99.97% metal weight purity, 3.0 μm average particle size, 55 m^2 g^{-1} surface area, from Alfa Aesar), battery-grade synthetic graphite nano-powder carbon black with high grade of crystallinity (C-NERGY Super C65 from Emerys, 62 m^2 g^{-1} surface area), PVdF-HFP or poly(vinylidene fluoride-*co*-hexafluoropropylene) (KynarFlex 2751-00 from Arkema), acetone (AR grade, 99.9% purity, Carlo Erba), LP30 (1 M $LiPF_6$ in 1:1 Ethylene Carbonate-Dimethyl Carbonate solution, Solvionic). All reagents and compounds were used without further purification and the proportions of each are indicated in Table 1. Slurries were prepared with varying amounts of CB and γ-Al_2O_3 and 10 wt% of PVdF-HFP as binder. PVdF-HFP was pre-dissolved with 3 mL of acetone for 1 h then all remaining powders were added with an additional amount of 3 mL acetone. Slurries were stirred overnight. The solvent was then evaporated under a fume hood and the resulting mixtures were thoroughly dried in an oven.

Pellets were made using a KBr Quick Press with a 2 mm die set both from International Crystal Laboratories, in order to fit the stacked pellets inside the NMR rotors which have 2.1 mm inner diameters. The powders were pressed twice and the resulting pellet's thicknesses were measured using an IP65 μm. The amount of materials was adjusted to obtain thicknesses between 0.130 and 0.140 mm while achieving a porosity of about 30%. The porosity was calculated from the bulk densities of each component and the corresponding equations can be found in the supporting information's section I. Conductivity measurements allowed us to characterize the carbon percolation and SEM microscopy provided information about the surface morphology. BET-BJH measurements (for Brunauer-Emmett-Teller and Barrett, Joyner et Halenda) were also performed to determine the macroporosity vs. mesoporosity proportion in the pellets and the measurements are provided in Table 1.

Due to space limitations, these parts are shown in the supporting information's sections II, III and V.

2.3. 1D quantitative NMR

The wetting of the model electrode was checked with NMR. Several sets of 10 pellets with a 4.5% CB content (sample 4) were soaked for varying times in an excess of LP30 electrolyte. The pellets were then placed in a 3.2 mm rotor. A 3.2 mm double resonance