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Pulsed-Field Gradient NMR Self Diffusion and Ionic Conductivity Measurements for Liquid Electrolytes Containing $LiBF_4$ and Propylene Carbonate

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ABSTRACT

Liquid electrolytes have been prepared using lithium tetrafluoroborate ($LiBF_4$) and propylene carbonate (PC). Pulsed-field gradient nuclear magnetic resonance (PFG-NMR) measurements were taken for the cation, anion and solvent molecules using lithium (^{7}Li), fluorine (^{19}F) and hydrogen (^{1}H) nuclei, respectively. It was found that lithium diffusion was slow compared to the much larger fluorinated BF_4 anion likely resulting from a large solvation shell of the lithium. Ionic conductivity and viscosity have also been measured for a range of salt concentrations and temperatures. By comparing the measured conductivity with a ideal predicted conductivity derived from the Nernst-Einstein equation and self diffusion coefficients the degree of ionic association of the anion and cation was determined and was observed to increase with salt concentration and temperature. Using the measured viscosity and self diffusion coefficients the effective radius of each of the species was determined for various salt concentrations.

1. Introduction

Liquid electrolytes are of scientific interest due to their use in electrochemical devices, they consist of an ionic salt dissolved in a solvent. The choices of these materials play a vital role in determining the dynamics of the ions in solution. Usually lithium based salts are chosen due to the high charge density that the lithium ions possess. The anion is usually chosen to be relatively large in size to create an uneven charge distribution, which promotes ionic dissociation. Since the primary application of liquid electrolytes is in electrochemical devices it is important for the ions to be relatively mobile and free to conduct, therefore a low ionic association is desired in these systems. In this study lithium tetrafluoroborate ($LiBF_4$) was dissolved in propylene carbonate (PC) at molar concentrations between 0.1–1.5 M (mol dm^{-3}), which corresponded to molal concentrations between 0.08–1.37 mol kg^{-1}. The aim of this current research is to probe the motion of the ions in solution as a function of both temperature and salt concentration. A secondary aim of this paper is to pave the way for future publications on polymer gel electrolytes; which involve adding polymer to a liquid electrolyte at high temperatures to form a porous polymer network filled with liquid electrolyte.

Following the pioneering research of Wright [1] and Armand [2] into solid polymer electrolytes and their potential for use in lithium batteries, thermo-reversible polymer gel electrolytes (PGEs) [3,4] have been studied at the University of Leeds with the introduction of solvents [5,6]. These gel electrolytes combine the high ionic mobility of conventional liquid electrolytes with the mechanical advantage of incorporating a polymer. Typical PGEs comprise of poly(vinylidene) fluoride (PVDF), propylene carbonate (PC) and lithium salts [7,8]. A first stage in developing a fundamental understanding of these gel electrolytes has been to study the behaviour of model liquid electrolyte solutions. Understanding the transport properties of these liquid electrolytes is important to use as a basis of comparison. Therefore in this paper the pure liquid electrolyte system is reported which will aid in the understanding of future papers concerning polymer gel electrolytes.

The experimental techniques which have been used to understand the dynamics of the current system are pulsed-field gradient NMR, dielectric spectroscopy and viscosity measurements. NMR has been proven to be a valuable tool for understanding the dynamics of liquid solutions via different techniques. In a previous publication it has been shown that the use of NMR relaxation times

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yield valuable information about the rotational and translational motion of the ions in solution [9]. In this paper pulsed-field gradient NMR was used in order to measure the translational self diffusion constants. It is possible to isolate individual nuclei using the corresponding resonant frequency. In this paper results for ^{1}H, ^{7}Li and ^{19}F nuclei have been measured which corresponds to the solvent molecules, lithium cation and fluorinated BF_4 anions, respectively. Therefore measuring the diffusion constant in this manner can yield information about the dynamics of each constituent within the liquid electrolytes; and these have been observed with changing temperature and salt concentration. Pulsed-field gradient NMR measurements have been carried out elsewhere on $LiBF_4$/PC systems for both liquids and polymer gel electrolytes [10,11]; however usually covering many samples over a small number of concentrations and temperatures.

Dielectric spectroscopy has been employed to measure the ionic conductivity of the liquid electrolytes. The ionic conductivity of an electrolyte is of scientific interest due to the primary application of these solutions as electrochemical devices; which require high conductivities to adequately perform. Detailed research into liquid electrolytes containing $LiBF_4$ have been measured elsewhere with carbonated solvents such as propylene carbonate and their mixtures [12–15]. In these papers many salt concentrations and temperatures have been probed and have a main emphasis on covering a large range of solvent mixtures. In the research presented here a single salt and solvent system was chosen in order to understand the core principals of the dynamics of the individual constituents. It should also be noted that in this research a conductivity cell was used which are commonly used in solid or gel research. The reason for choosing such a technique was in order to later compare the polymer gel electrolyte conductivity which were measured using the same conductivity cell. This paper will not only consider the conductivity at many different temperatures and salt concentrations, but will compare these results with the diffusion constants which allow a more in depth study of the dynamics and solvation of the ions in solution than previously reported.

Viscosity measurements were also taken at various temperatures and salt concentrations. The viscosity of a liquid electrolyte directly affects the mobility of the ions and therefore the conductivity. The viscosity was measured using a standard Ostwald viscometer which relies on a calibration sample and measured density. The density of the liquid electrolytes was measured alongside the viscosity measurements using several volumetric flasks, which were housed in the same water bath as the viscometer. The use of the viscosity in this research was to determine trends in the average radius of the solvent molecules, lithium cations and fluorinated BF_4 anions. It is also suggested in this research that by fitting a simple exponential to the viscosity and diffusion data as a function of salt concentration that the trends in the effective radii can be determined.

It is commonly known that the ionic conductivity will be affected by the number of charge carriers that form neutral pairs. It is possible by using the Nernst-Einstein equation along with the translational diffusion constants to predict the conductivity; with the assumption that all charge carriers are unpaired and contributing to the conductivity. Therefore by comparing the predicted and measured conductivities it was possible to give an estimation of the degree of ionic association in the liquid electrolytes. Other methods have been employed to probe the ion-ion interactions such as Raman spectroscopy as well as using the Walden product and limiting molar conductivities [16,17], however the use of the Nernst-Einstein equation to predict conductivity was been proven to be effective for both liquid electrolytes [18–23] and polymer gel electrolytes [24–27] and has been shown to yield a good approximation of the ionic interactions.

2. Experimental

2.1. Sample Preparation

All samples were prepared in an oxygen-free nitrogen filled glove box. The liquid electrolytes were prepared by mixing $LiBF_4$ salt with PC solvent at molar concentrations of 0.1–1.5 M at room temperature with magnetic stirrer bars. In this study the salt concentration is expressed as salt molality rather than molarity; as molality is independent of temperature. The molar concentrations of 0.1–1.5 M corresponds to molal concentrations in the range of 0.08–1.37 mol kg^{-1}. The PC used was 99.7% anhydrous, both the PC and $LiBF_4$ were vacuum sealed from Sigma-Adrich. The liquid electrolyte samples for the NMR diffusion measurements were sealed into 10 mm glass tubes for the ^{19}F and ^{7}Li measurements and 5 mm glass tubes for the ^{1}H measurements. The tubes were sealed in the nitrogen atmosphere of the glovebox to avoid any moisture in the samples.

The conductivity samples were also sealed inside the cell while in the glovebox, to reduce the chance of any moisture entering the system. While inside the Novocontrol BS1200 conductivity rig there was a constant supply of nitrogen gas which kept the sample in a nitrogen atmosphere during measurements. Some preliminary measurements were taken for liquid samples that were left in the cell for extended periods of time before being measured; these measurements yielded the same results and therefore it was assumed that moisture in the atmosphere was not affecting the sample.

2.2. NMR Diffusion

NMR diffusion previously measured at Leeds [25] used a Stejskal-Tanner pulse sequence. Here the NMR pulse sequence used was a complex bipolar stimulated echo pulsed-field gradient (BPStE-PFG) originally designed by Cotts [28]. Cotts sequence was an adapted form of a Stejskal-Tanner pulse sequence which eliminates background magnetic fields and has been used here at Leeds in previous studies [8].

Background magnetic field gradients manifest due to inhomogeneities in the magnetic field. The use of bipolar pulses removes these background magnetic field gradients. This introduces the relation for intensity of signal in the form of;

$$I = I_0 \exp\left(-4\pi^2\gamma^2\delta^2G^2D\left(\Delta - \frac{\delta}{3}\right)\right) \tag{1}$$

where G is the gradient field strength, Δ is the time between subsequent gradient pulses, δ is the gradient pulse duration and D is the self diffusion coefficient. The NMR parameters used were $\Delta = 40$ ms, $\delta = 10$ ms and the time between radio frequency (rf) and gradient pulses was 1 ms [25]; these values were unchanged throughout the experiments. The diffusion experiments are two dimensional as they are performed multiple times each with a different value for the pulsed-field gradient strength G. As the gradient is increased the intensity would decrease and therefore by fitting equation 1 to the decay of intensity as a function of gradient strength the diffusion constants were determined. The software that was used was Bruker Topspin 1.5, this software contains a function that calculates the maximum gradient strength to be used depending on the value of the diffusion constant being measured. Between the application of each of the various gradient strengths a time was left in order for the magnetisation from the previous run to dissipate. This delay is known as the recycle delay and was set here to $5T_1$.

The three different nuclei used here were ^{1}H, ^{7}Li and ^{19}F which correspond to the solvent molecules, cations and anions, respectively. The diffusion coefficients were measured using a 400 MHz