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NMR self diffusion and relaxation time measurements for poly (vinylidene fluoride) (PVDF) based polymer gel electrolytes containing $LiBF_4$ and propylene carbonate

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ABSTRACT

Polymer gel electrolytes (PGEs) have been prepared using lithium tetrafluoroborate ($LiBF_4$), propylene carbonate (PC) and poly (vinylidene fluoride) (PVDF). Self diffusion coefficients have been measured using pulse field gradient nuclear magnetic resonance (PFG-NMR) for the lithium cation, BF_4 anion and solvent molecules using ^7Li, ^{19}F and ^1H nuclei, respectively. It was found that lithium ion diffusion was slow compared to the much larger fluorinated BF_4 anion, which is attributed to a large solvation shell around the lithium ions. The ^7Li and ^1H diffusion measurements also exhibited two unique environments for the diffusive species. The measurement of NMR transverse relaxation times has confirmed the presence of lithium ions in multiple phases as shown by the diffusion measurements.

1. Introduction

Polymer gel electrolytes (PGEs) are membranes which consist of a polymer, an organic solvent and a salt. Polymer electrolytes are the focus of much research due to their primary application of use in electrochemical devices and more specifically secondary lithium batteries. The first instance of conductive polymers for use as possible electrochemical devices were presented in research carried out by Armand [1,2] and Wright [3,4]. Since this early research into solid polymer electrolytes there has been significant research, which has resulted in the evolution of dry polymer electrolytes to polymer gel electrolytes which contain high levels of organic solvent, this evolution is detailed in several reviews of polymer electrolytes [5–8]. The introduction of an organic solvent increased ion mobility and thus ionic conductivity. These gels are considered important as they offer many properties that traditional lithium ion batteries do not exhibit, such as enhanced safety features (since polymer gel electrolyte batteries do not contain free liquid outside the polymer structure). PGEs are also highly flexible and versatile and are easily produced. Due to easy fabrication by an extrusion lamination method, patented at the University of Leeds, there is no need for external casing or a polymer separator used to stop electrodes shorting [9].

Conducting polymer electrolyte research at the University of Leeds was initiated by Bannister et al. [10], who showed that through the use of amorphous comb shaped polymers relatively high conductivities could be achieved, these comb shaped polymers consisted of methacrylate backbones and short poly(ethylene glycol) side chains and teeth [11]. The next approach explored at Leeds consisted of producing gel electrolytes from poly (N,N dimethylacrylamide) (PDMA), conductivities of around 10^{-4} S cm^{-1} were obtained at room temperature [12]. These high conductivities were achieved with lithium salts and including the incorporation of N,N dimethylacetamide (DMAc) as a plasticiser [12]. The promising conductivities values achieved here led to a major research programme exploring thermoreversible polymer gel electrolytes based on poly(vinylidene fluoride) (PVDF) for use in advanced secondary battery applications [13].

In this paper we describe thermo-reversible gels produced from PVDF, which was chosen as the host polymer due to it being chemically inert and stable under 4 V; which is required for battery applications. PVDF is a polar polymer and thus has a relatively high

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dielectric constant, which aids in ionic dissociation of the salt ions and therefore increases ionic conductivity. PVDF is a semi crystalline polymer, which forms non chemically cross linked junctions, allowing the resulting polymer gel electrolytes to be thermoreversible. The semi crystalline gels form crystalline junctions within the solution below the melting temperature. The crystalline junctions will enter a melt if the melting temperature is exceeded due to the absence of chemical cross-links. These distinct properties of PVDF have resulted in many publications on PGEs containing PVDF, as both the host polymer [13–18] and as part of co-polymer systems (such as PVDF-HFP) [19–22].

Research into solid polymer electrolytes by Armand [1,2] and Wright [3,4] using poly(ethylene oxide) (PEO) mixed with various lithium based salts, resulted in very low conductivities ($\approx 10^{-5}$). It was found that within these solid polymer electrolytes the ions located in the amorphous regions of the polymer were responsible for the conductivity [4]. In order to enhance the conductivity in the polymer gel electrolytes the location of the ions and the conduction mechanism must be understood. It is therefore the aim of this paper to address the location of the anion and cation within the gel structure.

The precise structure of the polymer gel electrolytes is dependent on many contributing factors. However, the gels are usually found to be formed from aggregations of spherulites, which are believed to contain highly ordered crystalline lamellae which are connected by amorphous polymer to form spherical structures. It has been found that the size and shape of the spherulites are highly dependent on the rate of cooling once the gel has been formed [23]. A paper by Shimizu et al [24] shows via SEM that gels produced using diethyl carbonate (DEC) produces rough edged spherulites, where as γ-butyrolactone (GBL) and propylene carbonate (PC) both produce smooth edged spherulites. Although the term spherulite is commonly used in the literature regarding the gelation process, it is not clear the means by which these spherulites are formed. It has been suggested by Chou et al. that the gelation is a four step process; nucleation and growth into spherical structures, aggregation of the spherical structures, diffusion controlled coarsening and finally Ostwald ripening [25]. Chou et al. [26] have suggested that the spherulites may not be crystalline and instead the structure of the gels consists of an aggregation of non crystalline spherulitic structure, however it has been observed by Voice et al. [13] at the University of Leeds that there are clearly crystalline regions within the polymer gel structure.

Since the primary application of these polymer gel electrolytes is for use in secondary lithium batteries, it is important to understand the location of the ions within the gels. $T_{1\rho}$ measurements carried out by Hubbard et al. [27] showed that PVDF based polymer gel electrolytes contain multiple phases including a crystalline lamellae phase, an inter-lamellae amorphous polymer phase, a solvated amorphous polymer phase and a pure liquid phase. These phases were determined by using NMR relaxation times using the hydrogen (^{1}H) nucleus which will therefore have detected the polymer and the solvent molecules [27]. However, it is important to understand the role of the salt ions as these are responsible for conduction. In this paper we discuss the possibility of the lithium ions being present in multiple phases of the gels and in a subsequent publication will link these results with conductivity data in order to show that there are likely at least two conduction mediums for the lithium ions [28].

In this paper we have used NMR self diffusion measurements to understand the mobility of the solvent molecules, lithium cations and BF_4 anions using ^{1}H, ^{7}Li and ^{19}F resonant frequencies, respectively. NMR diffusion measurements have been proven to be a useful tool in understanding the mobility in polymer gel electrolytes [29–32,16,33,34]. However, the possibility of multiple diffusive species of both the lithium ions and solvent molecules is discussed in this paper, which has previously been reported by us [18] and also in a publication by Magistris et al [17]. However, this paper will contain a more in depth observation of the NMR diffusion as a function of salt concentration, polymer concentration and temperature.

2. Experimental methods

2.1. PGE preparation

All samples were prepared in an oxygen-free nitrogen filled glove box, in order to reduce the moisture content within the sample. The liquid electrolytes were prepared by mixing $LiBF_4$ (lithium tetrafluoroborate) salt with propylene carbonate (PC) at different concentrations. The PVDF polymer was then added to the liquid mixture and heated to 433 K (160 °C). The weight percentage of polymer to solvent used was 0%wt (liquid electrolyte), 20%wt and 30%wt PVDF. The thermo-reversible gels were produced under high temperature (433 K) and stirring and allowed to cool at ambient temperature. The 99.7% anhydrous propylene carbonate and $LiBF_4$ from Sigma–Aldrich were used as received. The Solef®1015 PVDF used was supplied by Solvay chemicals and placed in the dry glove box before use.

2.2. NMR diffusion

The diffusion coefficients were measured using a 400 MHz Bruker AVANCE II NMR spectrometer. The NMR pulse sequence used was a complex bipolar stimulated echo pulse field gradient (BPStE-PFG) originally designed by Cotts [35]. The Cotts sequence is an adapted from the Stejskal-Tanner pulse sequence [36] which eliminates background magnetic fields. Background magnetic field gradients manifest due to inhomogeneities in the magnetic field. This produces cross terms of the applied magnetic gradients and the background magnetic gradients. This introduces the relation for intensity of signal in the form of Eq. (1).

$$I = I_1 \exp\left(- D_1 (2\pi\gamma\delta G)^2 \left(\Delta - \frac{\delta}{3} \right) \right) \tag{1}$$

where G is the gradient field strength, Δ is the time between subsequent gradient pulses and δ is the gradient pulse duration. The introduction of bipolar pulses resolves the problem of the background magnetic field and allows measurement of the self diffusion coefficients. Bipolar pulses are two gradient pulses of equal magnitude with opposite sign.

The different nuclei were isolated by applying radio frequency pulses corresponding to the resonant frequency of the nuclei. The duration of the $\pi/2$ pulses were 18.5 μs and 19.6 μs at a power level of 3 dB for ^{7}Li and ^{19}F, respectively. The NMR parameters used were $\Delta = 40$ ms, $\delta = 10$ ms. These values were used as they have been proven to work with this type of measurement elsewhere [37].

2.3. Transverse relaxation times

The transverse relaxation times were measured on a Bruker 400 MHz AVANCE II Ultrashield NMR spectrometer for the ^{7}Li ^{19}F measurements and a 50 MHz Maran bench top NMR spectrometer for the ^{1}H measurements. The $\pi/2$ pulses were set as 18.5 μs and 19.6 μs at a power level of 3 dB for ^{7}Li and ^{19}F, respectively. The bench top NMR spectrometer was only capable of measuring using the ^{1}H resonant frequency, the pulse duration was set as 3.5 μs.

Both spectrometers used 10 mm diameter glass tubes. Due to the viscous nature of the resulting polymer gel electrolytes, the