Measuring Ionic Conductivity in Electrodes Prepared by Solvent-free Melt Extrusion

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Supporting Information

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Experimental

Electrolyte Preparation

Thermoplastic vulcanizate electrolytes were prepared via a solvent-free dynamic crosslinking technique as detailed in a previous publication.[1] Electrolytes comprised of 50/50 vol% of PCL (Sigma Aldrich, 80000 M) and EPDM (Saft) were prepared. LiTFSI (CapChem) was added such that the mass of the salt was 24.5 % of the total mass of the polymers. Luperox DI (Arkema), a crosslinking agent, was added in a proportion of 3 g per 100g of EPDM. The extruded material was flattened then calendered to a thickness of 200 µm. All samples were dried for twelve hours under vacuum at 60 °C prior to use.

Electrode Preparation

Electrodes were prepared by combining the TPV electrolytes described above with conductive carbon additives (carbon black and/or carbon nano fiber) and an active material, either $LiFePO_4$ (LFP) or $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC111) as described in Table 1 (main manuscript). Polymeric binder, the active material and the carbon additives were combined using a micro compounder (MC 15 HT from Xplore). The materials were mixed at 100 °C at a rate of 50 rpm for a total of twenty minutes. Further homogenization of the electrolyte materials was done using an open two-roll mill compounder (Scamex) at 50 °C. Electrodes were then calendered to a final thickness of 100 µm. All electrodes were dried for twelve hours under vacuum prior to use. Sample water content was 1000-2000 ppm as determined using a Computrac Vapor Pro XL (Arizona).

Electronic Conductivity Measurements

Electronic conductivity measurements were performed under ambient conditions using an Ossila four-point probe.

Ionic Conductivity Measurements

Ionic conductivity was measured using a SP-300 potentiostat (BioLogic) with a frequency range of 7 MHz to 100 mHz and an amplitude of 10.0 mV. All measurements were performed at 60 °C with sample temperature being equilibrated for two hours prior to taking measurements. A stack comprising an electrode sandwiched between two TPV electrolytes was placed between two mylar rings with an outer diameter of 19 mm and an inner diameter of 12 mm, Model C as described in the main manuscript. All measurements used for model testing were performed at 60 °C. Ionic conductivity measurements that were taken for the determining that activation energies for ion transport in the electrodes were acquired in ten degree increments between 40 and 80 °C. The electronic conductivity of the TPV electrolyte was measured at 5.596 x 10^{-9} S/cm, confirming that the material is electronically insulating.

Ionic conductivity measurements on the MTZ were performed by inserting the Model C stack between two stainless steel blocking electrodes. This assembly was placed in a Controlled Environment Sample Holder from BioLogic that was sealed inside of the glovebox. An MTZ-35 impedance analyzer and Intermediate Temperature System from Biologic with scanned frequencies between 3.5×10^{7} Hz and 5×10^{-2} Hz and a voltage amplitude of 10.0 mV was used to acquire conductivity at 60° C. Samples were equilibrated at 60 °C for two hours prior to taking measurements. All ionic conductivity measurements were performed three times. These values were used to obtain the average conductivities and standard deviations that are reported in the manuscript.

Density measurements

The PCL-EPDM electrolytes are comprised of 50 vol % PCL, 50 vol % EPDM and 24.5 wt% LiTFSI with respect to the mass of both polymers. The density of the polymer electrolyte (d_p) was calculated below using Equation S1. The densities of PCL (d_{PCL}), EPDM (d_{EPDM}) and LiTFSI (d_{LiTFSI}) were 1.14 g/cm^3, 0.86 g/cm^3 and 1.33 g/cm^3 respectively.

$$\frac{1}{d_p} = \frac{m_{PCL}/m_p}{d_{PCL}} + \frac{m_{EPDM}/m_p}{d_{EPDM}} + \frac{m_{LiTFSI}/m_p}{d_{LiTFSI}} \quad (S1)$$

Where m_{PCL}, m_{EPDM} and m_{LiTFSI} are the masses of PCL, EPDM and LiTFSI in the mixture respectively. The total mass of the polymer is represented by m_p. The density of the PCL-EPDM polymer electrolyte was calculated to be 1.06 g/cm^3.

Density measurements were performed on electrode disks with a diameter of 12 mm using a YPK03 density determination kit (Sartoris) with a Practicum 224-1S analytical balance (Sartoris). The liquid measurements were performed by submerging the sample in ethanol. Theoretical density was calculated using Equation S2 where d_e is the total density of the electrode, m_p and d_p are the mass fraction and density of the polymer electrolyte, m_{AM} and d_{AM} are the mass fraction and density of the active material, m_{CB} and d_{CB} are the mass fraction and density of carbon black and m_{CNF} and d_{CNF} are the mass fraction and density of the carbon nanofibers.

$$\frac{1}{d_e} = \frac{m_p}{d_p} + \frac{m_{AM}}{d_{AM}} + \frac{m_{CB}}{d_{CB}} + \frac{m_{CNF}}{d_{CNF}} \quad (S2)$$

The density of the PCL-EPDM polymer electrolyte was calculated to be 1.06 g/cm^3. Densities of 3.34 g/cm^3 and 4.7 g/cm^3 were used for LFP and NMC respectively. The density of the carbon black and the carbon nanofibers was 2 g/cm^3.

Equivalent Circuit Fitting Parameters

The equivalent circuit model presented in Figure 3 contains five elements: an induction loop (L1) which represents the instrument wires, the resistance R2 which represents the instrument, the resistance R3 which represents the sum of the PCL-EPDM layers electronic insulating layers and the electrode and constant phase elements Q2 and Q3 which represent diffusion. The resistance attributed to the studied electrode was separated from that of the PCL-EPDM layers using the measured thicknesses of each component and the known ionic conductivity of PCL-EPDM. The fits obtained for samples PCL-EPDM-1 through -4 are presented in Table S1.

Table S1: Equivalent circuit fits for electrode formulations containing 60 wt% active material

Formulation:	**PCL-EPDM-1**
L1	0.881 x 10^{-6} H
R1	15.9 Ω
Q2	0.118 x 10^{-9} F
R2	3118 Ω
Q3	1.94 x 10^{-6} F
Formulation:	**PCL-EPDM-2**
L1	0.704 x 10^{-6} H
R1	10.71 Ω
Q2	0.116 x 10^{-9} F
R2	3963 Ω
Q3	1.44 x 10^{-6} F
Formulation:	**PCL-EPDM-3**
L1	0.752 x 10^{-15} H
R1	19.3 Ω

Q2	0.12 x 10^{-9} F
R2	4776 Ω
Q3	1.06 x 10^{-6} F
Formulation:	**PCL-EPDM-4**
L1	0.782 x 10^{-6} H
R1	14.5 Ω
Q2	0.126 x 10^{-9} F
R2	3527 Ω
Q3	1.58 x 10^{-6} F

Electrode Density

Electrode density was measured by weighing samples in air and ethanol using a density determination kit. The measured densities were compared to the theoretical densities which were calculated using Equation S2. The measured and theoretical densities matched for the samples that were prepared using 60 wt% active material (Table S2), indicating zero porosity. The measured densities were lower than the theoretical densities for the samples prepared with 75 wt% active material which suggests the presence of some porosity.

Table S2: Comparison of measured and theoretical electrode densities

Sample	Measured Density (g/cm^3)	Calculated Density (g/cm^3)	Difference (%)
PCL-EPDM-1	2.22	2.26	1
PCL-EPDM-2	2.28	2.26	0.9
PCL-EPDM-3	1.99	2.02	1
PCl-EPDM-4	2.04	2.02	1
PCl-EPDM-5	2.52	2.68	6
PCL-EPMD-6	2.53	2.68	6
PCL-EPDM-7	2.74	2.85	4
PCL-EPDM-8	2.75	2.85	4

Activation Energy

Activation Energy was calculated using the Arrhenius method (Figure S1). Ionic conductivity was measured in ten degree increments between 40 and 80 °C using the method described above. Activation energy was found to depend only on the presence of carbon nanofibers with samples

PCL-EPDM-2 and PCL-EPDM-8 which contain carbon nanofibers having the same activation energy as the polymer electrolyte whereas activation energy was reduced in the samples prepared without carbon nanofibers (Table S3). This suggests that the absence of carbon nanofibers impacts the mechanism of lithium ion conduction in the PCL-EPDM matrix within the electrode.

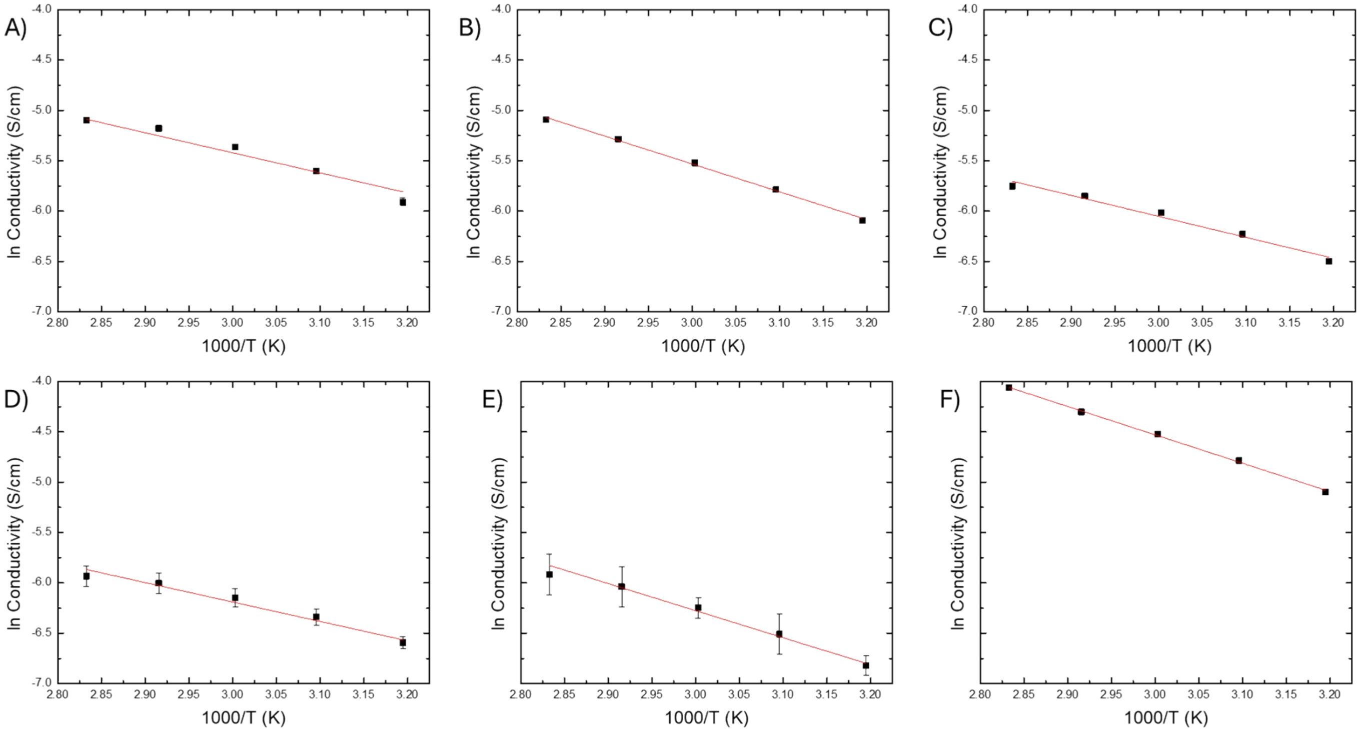

Figure S1: Arrhenius plots prepared based on ionic conductivity data acquired between 40 and 80 °C for PCL-EPDM-1 (A), PCL-EPDM-2 (B), PCL-EPDM-5 (C), PCL-EPDM-7 (D), PCL-EPDM-8 (E) and PCL-EPDM (F).

Table S3: Activation energy of PCL-EPDM-based electrodes calculated via the Arrhenius method between 40 and 80 °C

Sample	Activation Energy (eV)
PCL-EPDM-1	0.17 ± 0.02
PCL-EPDM-2	0.24 ± 0.01

PCL-EPDM-5	0.18 ± 0.01
PCL-EPDM-7	0.17 ± 0.01
PCL-EPDM-8	0.231 ± 0.007
PCL-EPDM	0.242 ± 0.002

References

1 L. Caradant, G. Foran, D. Lepage, P. Nicolle, A. Prébé, D. Aymé-Perrot and M. Dollé, Harnessing melt processing for the preparation of mechanically robust thermoplastic vulcanizate electrolytes, *J. Power Sources Adv.*, 2024, **28**, 100149.