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Ion transport restriction in mechanically strained separator membranes

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HIGHLIGHTS

- We model and measure the resistance increase associated with separator deformation.
- We show a Bruggeman relation can model tortuosity changes in deformed separators.
- We measure the α and γ Bruggeman parameters for monolayer separator membranes.
- We measure *in situ* the impedance changes in a pouch cell under applied compression.

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ABSTRACT

We use AC impedance methods to investigate the effect of mechanical deformation on ion transport in commercial separator membranes and lithium-ion cells as a whole. A Bruggeman type power law relationship is found to provide an accurate correlation between porosity and tortuosity of deformed separators, which allows the impedance of a separator membrane to be predicted as a function of deformation. By using mechanical compression to vary the porosity of the separator membranes during impedance measurements it is possible to determine both the α and γ parameters from the modified Bruggeman relation for individual separator membranes. From impedance testing of compressed pouch cells it is found that separator deformation accounts for the majority of the transport restrictions arising from compressive stress in a lithium-ion cell. Finally, a charge state dependent increase in the impedance associated with charge transfer is observed with increasing cell compression.

1. Introduction

The lithium-ion battery is the preferred energy storage technology in many applications spanning a wide range of size scales from portable electronics to electric vehicles to potentially grid level storage [1]. In many of these applications the battery cells are subjected to mechanical stresses as a result of manufacturing processes (e.g. stack pressure to maintain intimate contact between components [2]), normal operation (e.g. electrode expansion during charge [3] and SEI growth [4]), and abuse during service (e.g. external loading [5]). These stresses occur at the cell level and are distinctly different from the stresses that arise within individual electrode particles, being exerted on the electrode/separator stack normal to the plane of the electrodes. An understanding of cell-level mechanical stresses becomes even more important when one considers the push to higher capacity electrode materials which exhibit significant lithiation expansions (e.g. 400% for Si [6]).

While there have been a number of studies on stress evolution and fracture within individual electrodes and electrode particles [7–11], only recently have a limited number of studies considered the mechanical behavior of the lithium-ion cell as a whole [12–14]. Computational studies on lithium-ion cells in the literature that have included mechanical phenomena have generally concluded that mechanical stresses have only a small effect on electrochemical performance [15–17]. However, it has recently been demonstrated through ex-situ electrochemical studies of transversely compressed pouch cells that mechanical stresses can result in separator deformation, resulting in a significant degradation of cell performance [12]. Battery cells designed for long service lives and operation at high temperatures provide environments where substantial separator deformation can occur as a result of mechanical creep. The importance of the effects of mechanical and thermal stimuli on separators has indeed been the motivation of recent studies on the mechanical behavior of separators [18,19].

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Here we investigate *in situ* the effects of compressive deformation on the performance of microporous polymer battery separators as well as whole lithium-ion pouch cells through EIS studies of mechanically stressed samples. It is found that applied mechanical compression results in increased cell impedance, which can result in a reduction in performance, especially in high power applications where even small resistances translate into sizeable voltage drops. This increase in impedance can be attributed to decreased ion transport arising from the deformation of both the separator and electrodes.

2. Experimental methods

2.1. Materials

The separator cells used to measure separator conductivity as a function of strain are constructed by sandwiching 32 layers of wetted separator between two stainless steel foil electrodes and heat sealing the sandwich in an aluminum laminate pouch. Multiple separator layers are used for two reasons: to increase the sensitivity of the impedance measurements by increasing the overall resistance of the separator stack in the cell and to increase the sensitivity of the strain measurements by increasing the overall thickness of the separator stack. The stainless steel foil electrodes are made by cutting the foil into 2.3 × 2.3 cm squares with 3 mm wide leads extending from each end as shown in Fig. 1. The pouch is large enough to accommodate electrolyte that is ejected from the separator pores during compression without building up hydrostatic pressure. Cell construction is performed under argon atmosphere, but testing is conducted in ambient atmosphere. No impedance increase is observed in the separator cells over a period of 24 h in ambient atmosphere indicating a good seal.

Five separators are used in this paper: Celgard 3501, 2400, 2320, and 2340 obtained directly from the manufacturer and GMB 500 mAh pouch cell separator which is removed from GMB 500 mAh LCO-C pouch cells, obtained from Powerstream Technologies, Inc. and manufactured by Guangzhou Markyn Battery Co., Ltd. Celgard 3501 and 2400 are monolayer polypropylene separators while Celgard 2320 and 2340 are trilayer separators containing a layer of polyethylene between two polypropylene layers. Celgard 3501 contains a surfactant coating which is removed by rinsing in DMC prior to separator use. The GMB separator is a monolayer polyethylene separator fabricated using a dry process, which was determined from FTIR spectra of the separator and SEM images. The electrolyte used in the separator cell experiments is 1 M LiPF6 in 1:1 (EC:DMC) by wt. obtained premixed from Novolyte Technologies. The conductivity of the electrolyte is measured to be 12.1 mS cm^{-1}.

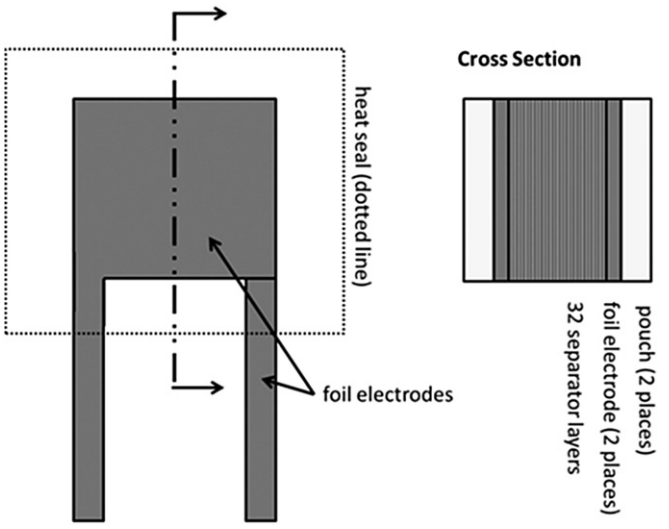

Fig. 1. Schematic of separator cell construction (not to scale).

2.2. Electrical & mechanical testing

All mechanical testing is performed using an Instron electromechanical universal testing machine. Load is applied using spherically seated compression platens to maintain good alignment and is measured using a 50 kN load cell. Strain is measured using the crosshead extension corrected for machine compliance. In order to obtain absolute values of cell thickness during the compression test, the crosshead extension is set to zero by compressing the platens together and zeroing the compressive extension prior to testing. To obtain consistent results, the separator cells are held at a compressive stress of 0.3 MPa until the impedance reaches a steady value. This ensures intimate contact between all separator cell components and allows thermal equilibrium to be reached prior to testing. All mechanical tests are performed using position control.

Impedance measurements are made with a Solartron 1287 electrochemical interface and a Solartron 1260 impedance analyzer using CorrWare Zplot software. Prior to each test, an EIS spectrum is taken to verify that the cell is in good condition. An AC signal of constant frequency is used to measure the real and imaginary components, Z' and Z'', of the AC impedance as a function of time. Z' as a function of strain is obtained by interpolating the strain–time data collected by the Instron Bluehill software to correspond to the impedance-time data collected by the CorrWare Zplot software.

2.3. Porosity measurement

Porosity here is defined as the void volume divided by the nominal volume of the separator. The nominal volume is the separator thickness l multiplied by the cross sectional area A and the void volume is the difference between the nominal volume and the actual volume of the polymer material comprising the separator. The polymer material volume can be determined by dividing the mass m of the separator sample by the density of the polymer material ρ_m. Thus separator porosity Φ is given by

$$\Phi = \frac{lA - \frac{m}{\rho_m}}{lA} \quad (1)$$

When calculating the initial porosity Φ_0 of the separator, an important parameter in subsequent discussion, the initial separator thickness used in Eq. (1) is the separator thickness as determined by Instron platen separation at the onset of the compression test. The polymer material density used in the porosity calculations is the density corresponding to 40% crystallinity, which is the percent crystallinity determined from latent heat measurements of separators made with differential scanning calorimetry [20].

3. Theoretical strain-induced separator resistance changes

3.1. Model development

To interpret the experimentally observed impedance changes associated with separator strain, a model assuming compression of a separator made of incompressible material is developed. Note that it is separator strain, not stress, which is directly responsible