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A High Performance Ceramic-Polymer Separator for Lithium Batteries

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ABSTRACT

A three-layered (ceramic-polymer-ceramic) hybrid separator was prepared by coating ceramic electrolyte [lithium aluminum germanium phosphate (LAGP)] over both sides of polyethylene (PE) polymer membrane using Electron beam physical vapor deposition (EB-PVD) technique. Ionic conductivities of membranes were evaluated after soaking PE and LAGP/PE/LAGP membranes in a 1 molar (M) lithium hexafluoroarsenate (LiAsF₆) electrolyte in ethylene carbonate (EC), dimethyl carbonate (DMC) and ethylmethyl carbonate (EMC) in volume ratio (1:1:1). Scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques were employed to evaluate morphology and structure of the separators before and after cycling performance tests to better understand structure-property correlation. As compared to regular PE separator, LAGP/PE/LAGP hybrid separator showed: (i) higher liquid electrolyte uptake, (ii) higher ionic conductivity, (iii) lower interfacial resistance with lithium and (iv) lower cell voltage polarization during lithium cycling at high current density of 1.3 mA.cm⁻² at room temperature. The enhanced performance is attributed to higher liquid uptake, LAGP-assisted faster ion conduction and dendrite prevention. Optimization of density and thickness of LAGP layer on PE or other membranes through manipulation of PVD deposition

parameters will enable practical applications of this novel hybrid separator in rechargeable lithium batteries with high energy, high power, longer cycle life, and higher safety level.

KEYWORDS: Ceramic/polymer/ceramic hybrid separator, charge-transfer resistance, lithium plating/stripping, voltage polarization, dendrite proof separator, lithium batteries

1. INTRODUCTION

Lithium-ion batteries (LIBs) having high energy density, power density, long cycle life, as well as low memory effect, are widely used in various applications ranging from mobile electronics to automotive [1, 2]. Even though LIBs have transformed the electronics industry, the energy density, power density, cycle life and safety are inadequate for high-energy applications, such as all electric vehicles batteries, aircraft batteries, or batteries that can power heavy machinery or extend the working hours of the current batteries [3].

LIBs consist of lithium transition metal oxide cathode and carbonaceous anode, whereas Li batteries (Li-S, Li-O₂, and advanced LIBs) use Li metal as common anode and S, O₂ or transition metal oxides as cathode separated by a membrane containing a non-aqueous liquid electrolyte or solid/gel electrolytes. Solid/gel electrolytes perform both as separator and electrolyte. Functioning of LIBs involves reversible lithium extraction from transition metal oxide host as the rechargeable cathode and into graphite as the anode host. Whereas functioning of Li batteries involves reversible extraction of lithium from lithium metal anode and into S, O₂ or transition metal oxide cathode. Micro-porous polyolefin separators, such as PE and polypropylene (PP) are commonly used in LIBs or Li batteries involving non-aqueous liquid electrolyte. Separator is a key component of LIBs or liquid-based Li batteries, and serves as a physical membrane that allows the transport of Li ions, but prevents direct contact between cathode and anodes.

Efforts have been made to improve separator performance (especially for liquid electrolyte-based LIBs) by solution coating of inorganics (Al_2O_3 , MMT, SiO_2 , etc.), along with binders on polymer separators (PE, PP, etc.) or by fabricating nanostructured polymer-/copolymer-inorganic mix by various techniques, such as electrospinning or fabricating alumina- or alumina/phenolphthalein polyetherketone-based, etc., porous ceramic membranes [4-11]. Liang, *et. al.*, [12] developed electrospun fibrous composite of Li^+ ion conducting inorganics (lithium lanthanum titanate oxide) with polyacrylonitrile (PAN) that showed higher liquid uptake, higher ion conductivity, higher electrochemical stability and overall improvement on cell performance. Solid electrolytes based on polymer, ceramic, and polymer-ceramic composites have proven to be promising as separators as well as electrolytes for batteries beyond LIB [13-15]. Polymer and gel electrolytes can be fabricated in thin film form but they are unable to stop dendrite growth completely. In addition to high Li^+ ion conductivity, ceramic solid electrolytes, such as LAGP (5 mS/cm at 23 °C) [14] or lithium aluminum titanium phosphate (LATP) (3 mS/cm at 25 °C) [16] combines many favorable properties such as solid-state nature, broad electrochemical window (>5 V), negligible porosity and single ion conduction (high transference number, no dendrite formation, no crossover of electrode materials to opposite side of electrodes compartment, etc.,) enabling high-energy battery chemistries and mitigating safety and packaging issues of conventional lithium batteries [15].

In present work, ultrathin layer (≈ 130 nm) of superionic conducting ceramic (LAGP) has been deposited on both sides of PE separator by using EB PVD technique. The goal was to obtain thin film of single ion (Li^+) conductor on mechanically-stable membranes that not only have the basic functions of battery separator, but also can conduct lithium ions and prevent Li dendrite growth, which can significantly improve the battery kinetics and cycle life. LAGP solid ceramic

electrolytes that possesses high ion conductivity [14] was used as the single Li^+ ion conducting ceramic to stop dendrite formation and growth during Li cycling. Results show that the coating of LAGP onto PE membrane can combine the advantageous properties of both components (PE and LAGP) and lead to a new hybrid separator that has high mechanical strength, large liquid electrolyte uptake, high ionic conductivity, good electrochemical stability, improved safety, reduced electrode–electrolyte interface resistance and low Li stripping/plating voltage polarization. As a result, the new LAGP/PE/LAGP hybrid membranes can provide ideal structures and properties for separating electrodes, supporting electrolytes, and transporting lithium ions. Lithium-ion cells using these membrane separators can achieve good battery performance, such as large capacity, good cycleability, high-rate capability, and enhanced safety.

2. EXPERIMENTAL DETAILS

2.1. PREPARATION OF THE HYBRID MEMBRANE

LAGP target material for fabricating hybrid membrane was prepared following our earlier procedure [14]. First, LAGP glass with molar composition $19.75\text{Li}_2\text{O}\cdot 6.17\text{Al}_2\text{O}_3\cdot 37.04\text{GeO}_2\cdot 37.04\text{P}_2\text{O}_5$ was synthesized through solid-melt reaction at 1350 °C by using reagent-grade chemicals such as Li_2CO_3 (Alfa Aesar), Al_2O_3 (Aldrich), GeO_2 (Alfa Aesar), and $\text{NH}_4\text{H}_2\text{PO}_4$ (Acros Organics). Subsequently, LAGP glass was crystallized at 850 °C for 12 hours, which is hereafter called LAGP ceramic for developing 3D ion conducting structure. The measured bulk ion conductivity of this LAGP composition was found to be $\approx 5 \text{ mS}\cdot\text{cm}^{-1}$ at room temperature [14]. Even though, the ionic conductivity of LAGP is high, it cannot be used as an electrolyte with energy dense Li metal anode. This is because of the high level of chemical reactivity of LAGP, similar to other LiSICON ceramic electrolytes, when in direct contact with Li metal [17]. A possible solution to this chemical reactivity issue is to put a thin stable film at the Li/LAGP interface. For example, West et al. [18] suggested that a LiPON-coated LATP plate is chemically stable against Li metal. Kumar

et al. [19] used lithium oxide/boron nitride based polymer-ceramics composite to stabilize Li/LAGP interface. In the present investigation liquid electrolyte (LiAsF_6 in EC:EMC:DMC) including vinylene carbonate (VC) has been used as interface layer between Li and LAGP to stabilize Li/LAGP interface. The use of VC for lithium metal anode suppresses the deleterious reaction between the deposited lithium (during lithium cycling) and the electrolyte [20].

A 130 nm-thick LAGP film was deposited on both sides of PE separator (Celgard, MTI Corp.) using EB-PVD. The EB-PVD system has a multi-hearth high power electron beam source capable of evaporating most metals and ceramics at a fast rate. In this process, electrolyte material (LAGP) was placed in a graphite crucible. The cleaned substrate (PE) was mounted on a metal plate. The chamber was evacuated to a base pressure of $<10^{-6}$ Torr. A deposition rate of 1.0-1.5 nm per/second was used to deposit ≈ 130 nm LAGP film on one side of PE separator and then on the other side. The deposition parameters can be manipulated to obtain LAGP film of desired thickness, density/porosity. As prepared LAGP/PE/LAGP functional separator was used for the current investigation without further treatment. It is noteworthy to mention here that the flexibility of LAGP/PE/LAGP separator was similar to the PE separator. Separator in the form of a disc was punched out and used in the present investigation. Punching the separator may damage the edges and there may be risk of potential short circuit. Keeping this possibility in mind we have used larger size separator as compared to electrodes (Li or SS) in order to avoid short circuit risks that may arise from damaged separator edges. The diameter of separator and electrode used were 17 mm and 16 mm, respectively.

2.2. CHARACTERIZATION OF HYBRID MEMBRANE

Coin cells were fabricated to determine electrochemical impedance spectra of PE and hybrid separators using stainless steel (SS) electrodes (SS/separator-1M LiAsF_6 /EC-DMC-EMC/SS). In addition, coin cells were fabricated using pure lithium metal as electrodes to

determine Li plating and stripping (Li/separator-1M LiAsF₆/EC-DMC-EMC/Li). The liquid electrolyte used in the present investigation includes 2% vinylene carbonate (VC). Coin cells were assembled in a ultra-pure glove box (O₂, H₂O < 1 ppm) glove box (Pure Lab^{HE} Innovative Technology, Industrial Way, Amesbury, MA 01913). Electrical and electrochemical performance of cells were evaluated using a Solartron SI 1287 electrochemical analyzer in conjunction with a SI 1260 Impedance/gain-phase analyzer. Electrochemical impedance spectroscopy (EIS) of the cells was conducted over a frequency range 0.1 Hz to 10⁶ Hz. Li stripping-plating measurements on Li/Li symmetrical cells were performed in a galvanostatic mode with a constant current density 1.3 mAcm⁻². Surface morphologies of PE and hybrid separator were examined using SEM. The XRD patterns were collected between 2θ = 15° to 80° on (Rigaku D/MAX) fitted with CuKα radiation source.

3. RESULTS AND DISCUSSIONS

Figure 1 shows impedance plots (a- @ 23 °C, b- @ 85 °C) and the Arrhenius plot (c @ 23 °C) of PE and LAGP/PE/LAGP separators in 1M LiAsF₆/EC-DMC-EMC electrolyte. The diameters of separators and SS electrodes are 1.7 cm and 1.6 cm, respectively. The size of the separator is larger than the size of SS electrodes to avoid any electrical shorting and eliminating potential debris produced damage during separator cutting. A common active area between separator and SS electrodes equal to 2 cm² has been considered for conductivity measurement. The high frequency Z' intercept (Fig. 1 a, & b) was used as the bulk electrolyte impedance. The value of impedance (in Ω) was normalized with samples common area (A = 2 cm²) and thickness of separators (Celgard t = 25 μm; LAGP/celgard/LAGP t = 25 μm + 130x2 nm (thickness of LAGP coating)) to calculate conductivity (σ = (t/A)*(1/impedance)). Before impedance measurement test samples were stabilized at various temperatures including 23°C using an environmental chamber

for 1 hour. The hybrid separator shows lower impedance as compared to PE separator (Figures 1(a) and (b)). The hybrid separator (LAGP/PE/LAGP) exhibits increased ionic conductivity in the entire temperature range (23-85 °C) (Figure 1(c)). The decrease in impedance and increase in ionic conductivity in the functional separator can be attributed to higher electrolyte uptake (EU) (≈ 20 wt. %) and added ionic contribution from LAGP component of the hybrid separator. The EU was calculated by the formula: $EU (\%) = ((W_f - W_0)/W_0) \times 100$, where W_f and W_0 are the weights of the electrolyte-soaked and dry membrane separators, respectively. Due to the inorganic nature, the wettability of the polar liquid electrolyte (LiAsF₆/EC-DMC-EMC) with LAGP is expected to be higher than non-polar PE separator. When a drop of liquid electrolyte was introduced each on PE and LAGP/PE/LAGP separators, spreading and absorption of liquid was much faster in LAGP/PE/LAGP as compared to PE separator.

Figure 1.

A practical ceramic solid electrolyte (e.g., LAGP, LASnP, LASiP, LATP) would be a few microns thick, but dense enough to mechanically stop dendrite growth. The goal of this effort was to demonstrate a workable concept of using binder free thin, dense, pristine, single Li⁺ ion conducting LAGP layers on flexible structures and demonstrate improved electrochemical performance compared to the traditional PE or PP separators. Coin-type symmetric Li|Li cells with hybrid membrane and PE membrane soaked in LiAsF₆ electrolyte were fabricated to investigate dynamic (Li plating and deplating process) electrochemical stability of both these membranes. Figure 2(a) and 2(b) show SEM images of PE and LAGP coated PE membranes respectively. Figure 2(c) shows typical voltage profiles for the symmetric cell cycled in 1M LiAsF₆ electrolyte. It was observed that the hybrid membrane is highly stable in 1M LiAsF₆ for more than 300 cycles at current density of 1.3 mAcm⁻² with a high Li areal capacity (≈ 3 mAh.cm⁻²) during both Li

plating and deplating process. PE without LAGP coating not only leads to abrupt variation in polarization during initial Li plating and stripping, but also showed significant increase in voltage polarization as can be seen in Figure 2(c).

Figure 2.

Figure 2(c) shows significant lowering in Li/electrolyte-separator/Li symmetrical cell polarization after 300 cycles when LAGP film was deposited on both sides of reference polymeric separator (Figure 2(a)). Low cell polarization is required for energy delivery for a cell operating at high charge-discharge rate. Figures 2(a) and (b) show the high magnification SEM images of the porous PE membrane and the LAGP/PE/LAGP hybrid membrane. PE membrane has a uniformly interconnected highly porous structure (Figure 2(a), and is responsible for free dendrite growth and penetration. For the hybrid membrane, an uniform and dense coating of LAGP on the porous PE membrane is seen in Figure 2(b) that prevents growth of dendrites. The hybrid separator was used without any thermal treatment and few cracks were found. Post deposition annealing could potentially eliminate crack formation [14]. However, high temperature annealing/sintering to make single phase LAGP will require separator material other than PE or PP (such as high temperature carbon fiber or glass fiber) and will be of interest in future research.

In order to understand the different electrochemical behavior observed in Figure 2(c), the impedance of the cells (involving PE and hybrid separator) before and after Li plating and deplating was measured and are shown in Figure 3. Both before (Figure 3(a)) and after (Figure 3(b)) Li/Li cycling, LAGP-coated PE separator shows significantly lower cell resistance (electrolyte + and charge transfer resistance). The higher ionic conductivity shown in Figure 1(c) and lower cell impedance shown in Figure 3 are responsible for lower cell voltage polarization observed in Figure 2(c). Lower voltage polarization allows functioning of an electrochemical cell

at high charge-discharge current rate with negligible cell degradation.

Figure 3.

To further differentiate the behavior of PE and LAGP-coated PE separators the surface morphology and XRD after the 300th Li/Li cycle were investigated. Figures 4(a) and (b) show surface morphology of PE and LAGP/PE/LAGP separators, respectively after these separators were used for 300 cycles in Li/Li symmetrical cells (Figure 2(c)). If compared with surface morphology of pristine PE separator (Figure 2(a)) it is clear that during lithium cycling, the PE separators have accumulated significant amount of powder/debris on both sides of PE separator that completely filled the pores of original PE. The debris is the product of lithium and electrolyte reaction and fragmented lithium dendrites (lithium foil used at the start of cell fabrication was found to be powdery after 300 cycles) formed during cycling. In the case of hybrid separator only a small amount of powder (reaction product of lithium and electrolyte or lithium dendrites) was visually observed, most of the lithium remained intact (high usable Li content) in metallic form. As can be seen in Figure 4(b) surface of used LAGP/PE/LAGP separator is smooth as the original (Figure 2(b)). Preservation of original surface morphology of functional separator and only partial degradation of lithium foil used can be attributed to the ability of LAGP to prevent dendrite formation; thus prolonging cell cycling life (Figure 2(c)) and lower cell resistance (Figure 3) as compared to uncoated PE separator. Figure 4 (c) shows XRD pattern of 1-bulk LAGP, 2-used (300 cycles) PE and 3-used (300 cycles) LAGP/PE/LAGP separator. Characteristic peaks of LAGP are preserved even after 300 cycles, suggesting stability of LAGP material toward long-term and high current Li cycling. Smooth, dense, mechanically-stable, electrochemically-stable and dendrite proof characteristics shown by LAGP will prove beneficial for rechargeable Li batteries.

Figure 4.

4. CONCLUSIONS

An EB-PVD technique was used to fabricate ceramic/polymer/ceramic (LAGP/PE/LAGP) hybrid separator for rechargeable LIBs and Li batteries. It was found that the application of a ceramic electrolyte (LAGP) layer on traditional PE separator soaked in 1M LiAsF₆ liquid electrolyte combined the best attributes of traditional PE separator and solid inorganic electrolytes. The synergistic behavior of hybrid separator resulted in a high mechanical stability/flexibility, increased liquid uptake, high ion conduction, reduced cell voltage polarization, no lithium dendrite formation and increased usable lithium content as compared to the state-of-the-art PE separator used in LIBs. Optimization of thickness and density of LAGP or other LISICON ceramic electrolytes on PE or similar polymer separator along with post deposition annealing, will result in a functional separator that can be used to prolong life cycle and power capability of present LIBs. Thickness and density optimization of LAGP or LATP on polymer separators and their use in full Li battery (Li-S, Li-O₂ and Li anode-based LIB) cells are expected to further improve performance.

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FIGURE CAPTIONS

1. PE and LAGP/PE/LAGP soaked in 1M LiAsF₆/EC-DMC-EMC electrolyte. Electrochemical impedance spectra at (a) 23 °C, (b) 85 °C and (c) ionic conductivities in temperature range 23-85 °C.
2. SEM images of (a) PE and (b) LAGP-coated (130 nm) PE separators. (c) 300th cycle cell polarization of Li/Li symmetrical cells during Li plating-stripping at current density = 1.3 mA.cm⁻², using PE and LAGP-coated flexible separator/electrolyte. Both PE and LAGP/PE separators were soaked in 1M LiAsF₆ electrolyte and sandwiched between two Li foils for fabricating Li/Li half cells.
3. Electrochemical impedance spectra of Li/Li symmetric cells using PE and LAGP/PE/LAGP hybrid separator soaked in 1M LiAsF₆ liquid electrolyte: (a) before Li plating-stripping and (b) after 300th Li plating-stripping at 23 °C.
4. (a) and (b) surface morphology of PE and LAGP/PE/LAGP separator, respectively, after 300 cycles in a Li/Li symmetrical cell involving 1M LiAsF₆ liquid electrolyte. XRD pattern of same two separators are shown in Figure (3) (c).

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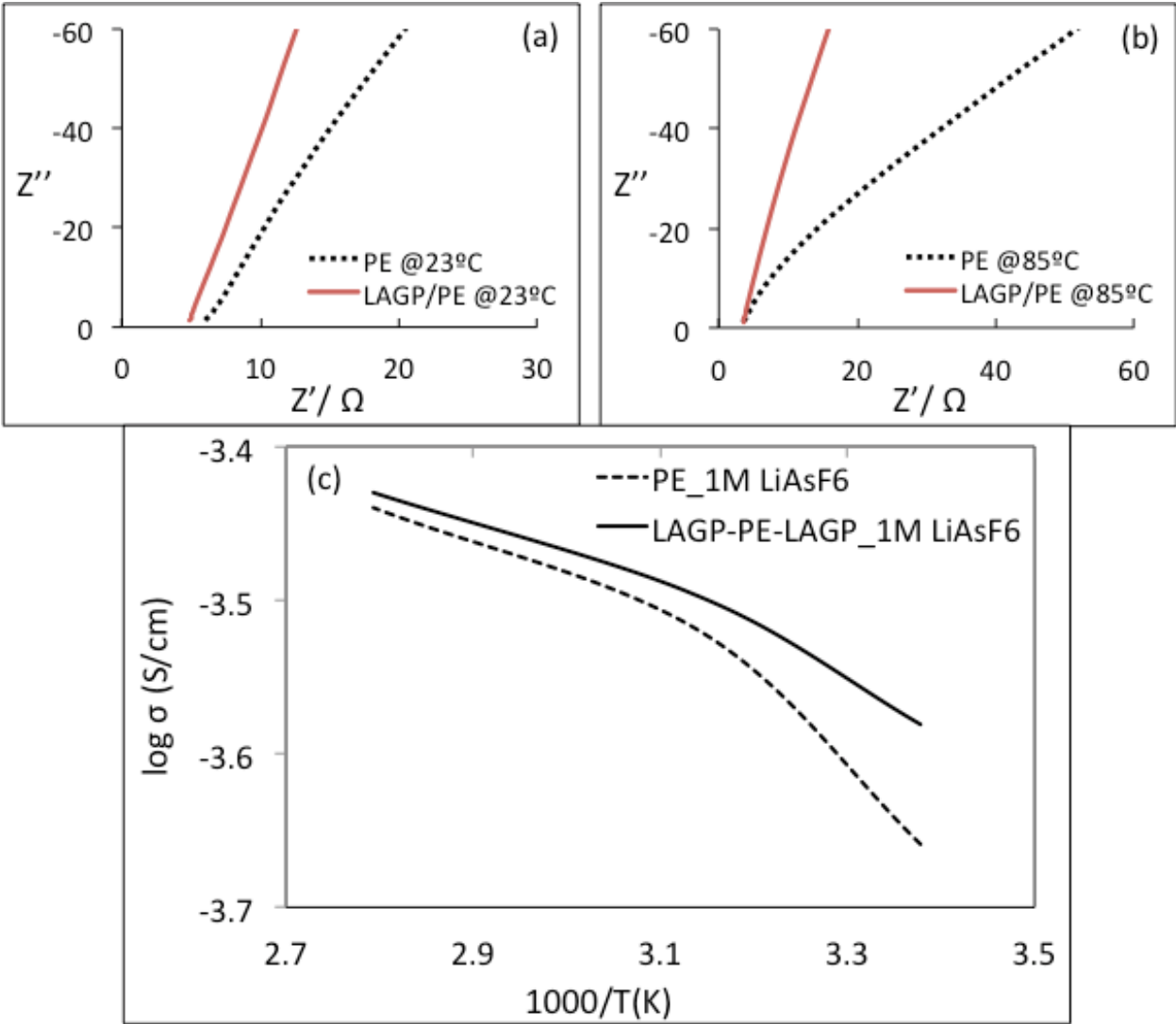


Figure 1

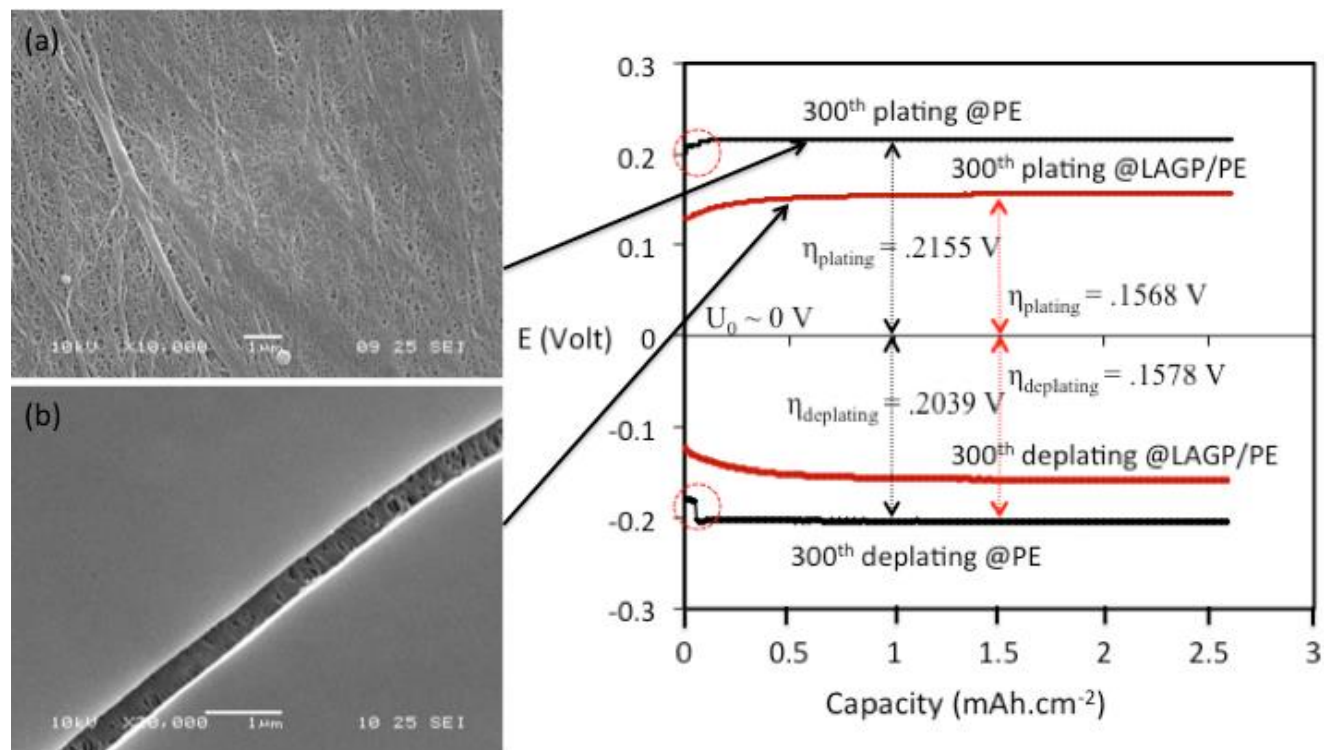


Figure 2

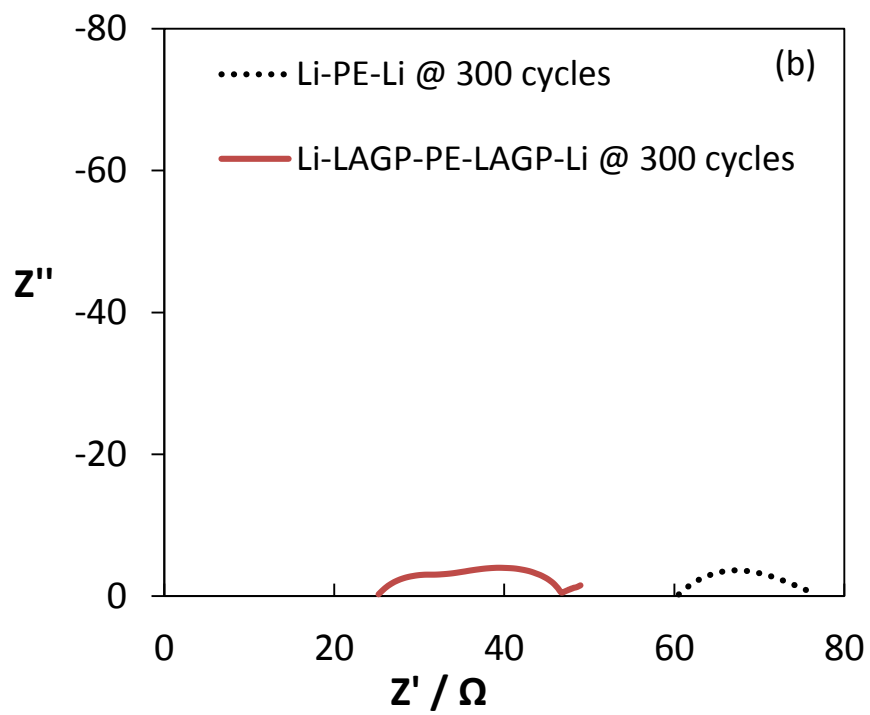
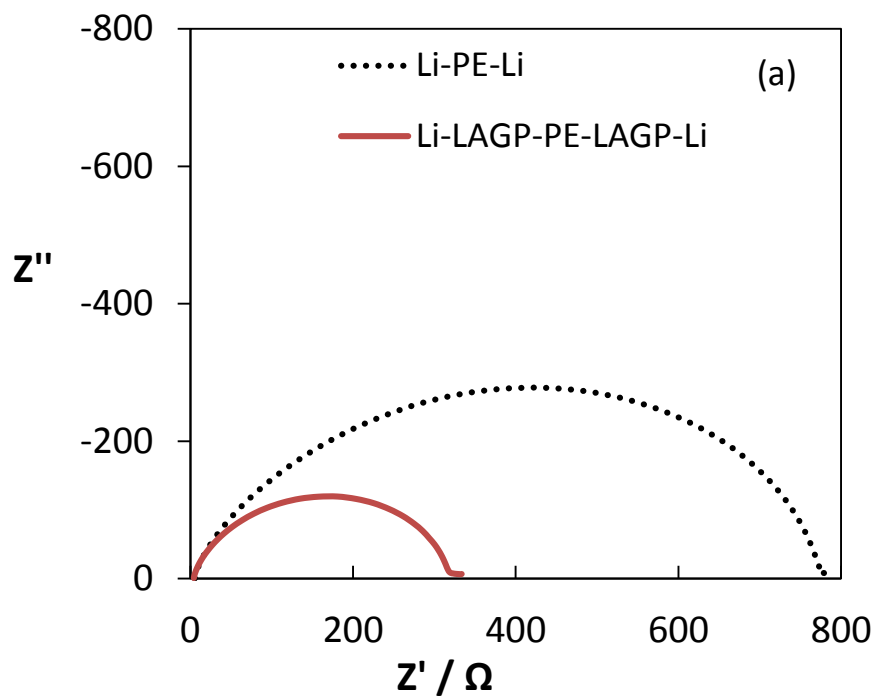


Figure 3

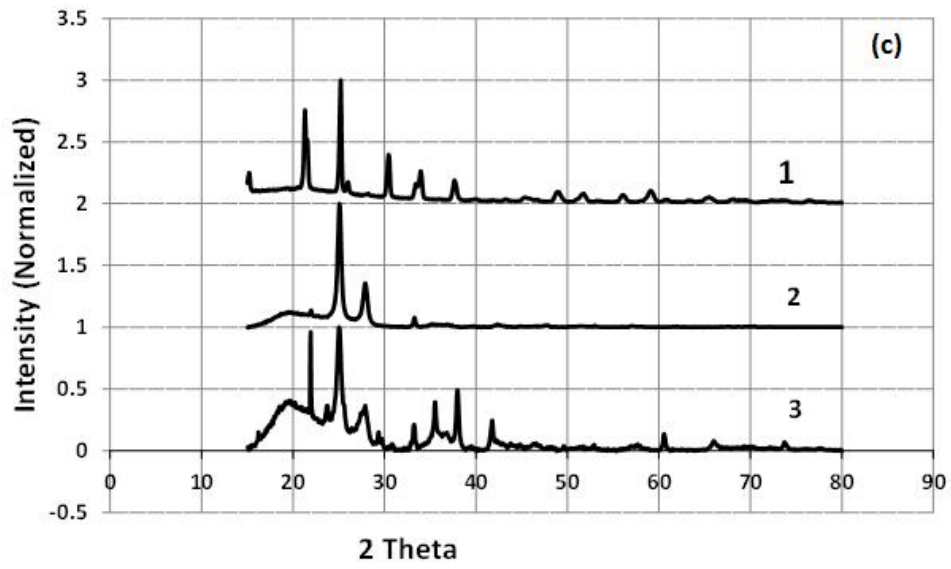
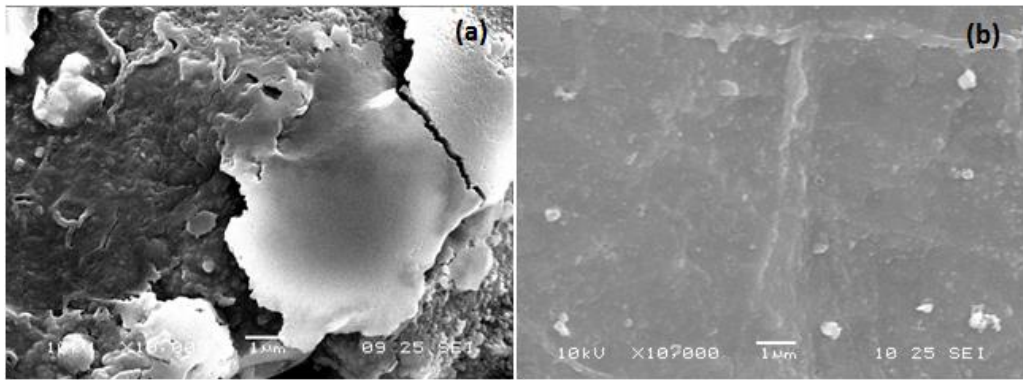


Figure 4.