ADVANCED GEL POLYMER ELECTROLYTE FOR LITHIUM-ION POLYMER BATTERIES

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ABSTRACT
We report improved performance of Li-ion polymer batteries through advanced gel polymer electrolytes (GPEs). Compared to solid and liquid electrolytes, GPEs are advantageous as they can be fabricated in different shapes and geometries; also ionic properties are significantly superior to that of solid and liquid electrolytes. We have synthesized GPE in form of membranes by trapping ethylene carbonate and propylene carbonate in a composite of polyvinylidene fluoride and N-methylpyrrolidinone. By applying phase-transfer method, we synthesized membranes with micro-pores, which led to higher ionic conductivity. The proposed membrane is to be modified further to have higher capacity, stronger mechanical properties, and lower internal resistance. In order to meet those requirements, we have doped the samples with gold nanoparticles (AuNPs) to form nanoparticle-polymer composites with tunable porosity and conductivity. Membranes doped with nanoparticles are expected to have higher porosity, which leads to higher ion mobility; and improved electrical conductivity. Four-point-probe measurement technique was used to measure the sheet resistance of the membranes. Morphology of the membranes was studied using electron and optical microscopies. Cyclic voltammetry and potentiostatic impedance spectroscopy were performed to characterize electrochemical behavior of the samples as a function of weight percentage of embedded AuNPs.

Keywords: gel polymer electrolyte, li-ion polymer, battery

INTRODUCTION
Since the 1960s, lithium secondary batteries have been used as power sources[1]. After several years of research efforts, lithium secondary batteries, especially lithium-ion polymer batteries (LIPBs), are now a major power sources for portable electronic equipment such as mobile phones, laptops, and even electric vehicles[2]. Success of LIPBs relies on numerous advantages including low cost, reliability, and durability[3]. Nowadays, with the rapid development of electronic equipment, there is a greater demand for energy storage systems; and LIPBs can meet these needs.

The design of a thin-film LIPB stands out among other LIPBs, because the thin-film features unique properties, which
includes a wide variety of shapes, easy assembly, and flexible structure. As shown in Figure 1, a thin-film LIPB typically consists of an anode, an electrolyte layer, and a cathode. In the long term, the improvements on anodes, electrolytes, and cathodes are all necessary for progress in LIPBs. Cathod and anode can be deposited on electrodes using variety of different methods. We have shown previously that polymers, metal nanoparticles, and their composites can be deposited on functionalized substrates using layer-by-layer deposition technique[4-10]. We have also demonstrated the influence of the nano and micro structures of thin-films on the electrical and ionic properties of the electrodes and functionality of MEMS devices[11-27]. However, the experiments discussed in this work focus on improving the gel polymer electrolyte (GPE) by studying gold nanoparticle (AuNP) doped GPEs for flexible LIPB.

Currently, four polymers are identified as most suitable materials for the backbone structure of GPEs: polyethylene oxide (PEO), polyacrylonitrile (PAN), polymethyl methacrylate (PMMA), and polyvinylidene fluoride (PVdF). Due to its excellent chemical stability, electrochemical properties, high affinity, and good mechanical properties, PVdF-based GPE is the most investigated structure for LIPBs[28]. Although exhibits promising performance, there is still room for improvement for PVdF-based GPEs. In order to form advanced GPEs, a group of researchers[29, 30] found that suitable ceramic fillers, such as silica, neutral alumina, acidic alumina, and basic alumina, enhance the mechanical stability and allow a long and more efficient cycling of the battery. To increase the ionic conductivity, reliability, and durability, gold nanoparticles[31] are discussed as filler for GPE in this paper.

Because of the polymer’s polymorphism and PVdF’s piezoelectric properties, lithium electrolytes can be stored in the approximately 50% amorphous structure, which is the result of PVdF being a semicrystalline polymer[32, 33]. In this case, GPE is synthesized in two steps: fabricating porous PVdF membranes and then doping the membranes with lithium-based electrolytes - lithium hexafluorophosphate (LiPF₆) in this work.

EXPERIMENTAL
Copper foil single-side coated by CMS Graphite (240mm L x 200mm W x 0.1mm t) was used as anode; aluminum foil single-side coated by LiMn₂O₄ (240mm L x 200mm W x 0.1mm t) was used as cathode (MTI Corporation). 1-Methyl-2-pyrrolidone (MP) (99.5%), ethylene carbonate (EC) (98%), propylene carbonate (PC) (99.7%), lithium hexafluorophosphate (LiPF₆) (98%), ethanol (99.5%), polyvinylidene fluoride (PVdF) were obtained from Sigma-Aldrich and used without further modifications; gold nanoparticles (AuNPs) (diameter 3.2nm, 99.9%, 20ppm aqueous) were obtained from Purest Colloids Inc and were used as received.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>L</td>
<td>length</td>
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<tr>
<td>W</td>
<td>width</td>
</tr>
<tr>
<td>D</td>
<td>diameter</td>
</tr>
<tr>
<td>σ</td>
<td>ionic conductivity</td>
</tr>
<tr>
<td>t</td>
<td>thickness</td>
</tr>
<tr>
<td>A</td>
<td>cross-sectional area</td>
</tr>
<tr>
<td>R_i</td>
<td>internal resistance</td>
</tr>
<tr>
<td>f_m</td>
<td>medium frequency</td>
</tr>
<tr>
<td>f_h</td>
<td>high frequency</td>
</tr>
<tr>
<td>f_l</td>
<td>low frequency</td>
</tr>
<tr>
<td>C_DL</td>
<td>double-layer capacitance</td>
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<tr>
<td>Z_im,m</td>
<td>medium imaginary impedance</td>
</tr>
<tr>
<td>R_s</td>
<td>solution resistance</td>
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<tr>
<td>R_{ct}</td>
<td>charge-transfer resistance</td>
</tr>
<tr>
<td>R_{b}</td>
<td>bulk resistance</td>
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<tr>
<td>ΔV</td>
<td>change of voltage</td>
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To make the AuNPs compatible with PVdF, the medium (water) was exchanged through a solvent exchange process as follow: Firstly, 40 mL original AuNPs solution was heated under 100°C. When the amount of solution decreased to 2mL, 1-Methyl-2-pyrrolidone (NMP) was added as the new solvent to increase the net volume to 22mL. The solution was heated again until 20mL was left. The solution was then sonicated for 60 minutes to re-disperse nanoparticles in the medium. Then, the resultant solution, a 40ppm homogeneous AuNPs in MP, was used for the experiments. Before and after the solvent exchange process, the property of solution was determined by ultraviolet absorbance spectroscopy.

As presented in Figure 2, the GPE is a membrane synthesized by trapping EC and PC plasticizers in PVdF and MP solutions and soaked in lithium hexafluorophosphate (LiPF₆).
Firstly, EC and PC with weight ratio 1:1 were mixed and heated at 110°C to dissolve completely. Then, PVdF was added to pure MP with weight ratio (1:3) as control group (solution 1); and PVdF added to 40ppm AuNP-MP solution with the same ratio as experimental group (solution 2). Two solutions were prepared individually, both solutions were heated together at 110°C and stirred on a magnetic stirrer until desired viscosity was reached. Then, the slurry was casted onto a flat glass disk. The flat glass disk with the slurry was then left at 80°C for 2 hours; then soaked in 10% ethanol solution for 12 hours. Then, a pale yellow membrane for control and a light purple AuNP-doped membrane for the experiments remained in the petri dish. The membranes in both groups with 0.3mm thickness were cut into 2cm x 2cm squares and were stored at ambient conditions. Finally, the membranes were activated by soaking into a 1M solution of LiPF₆ in EC:PC (1:1) for 24 hours under Argon.

The ionic conductivity of GPE was measured by impedance spectroscopy (VersaSTAT 4) using two steel chips (15.5mm D x 0.2mm t) as the blocking electrode cells. Impedance spectroscopy (1.0E5 Hz to 0.1 Hz, ΔV = 10mV) was periodically monitored over 30 days. The thin-film cell was assembled as shown in Figure 3; with GPE located in between the cathode and anode. In the actual model on the left of Figure 3, cathode and anode are exact 2cm x 2cm; but GPE film is larger than cathode and anode so the cell would not be shorted. The surface of protection cover that face inside of the cell is sticky, which helped airtight enclosure of the whole system.

![Figure 3: Structure of LIPB. Insets show photographic images of the actual structure.](Image 3)

**RESULTS AND DISCUSSION**

**Property of AuNPs:**
As presented in Figure 4, for any wavelength of Ultraviolet spectrum between 400nm and 800nm, the value of absorbance after solvent exchange is much greater than the value of absorbance before solvent exchange. This implies that the gold nanoparticles contained in a unit of solution are able to absorb more ultraviolet spectrum which translates to higher concentration.

![Figure 4: Comparison of the absorbance measured after solvent exchange (red line) with the absorbance measured before the solvent exchange (blue line) and absorbance measured by the AuNPs solution only evaporating](Image 4)

Overall, since the shapes of the three curves showed in Figure 4 are similar and the peaks are approximately at the same wavelength, one can conclude that AuNPs have kept their unique properties in NMP.

Nevertheless, by drawing a vertical line at the peak point of blue curve, it is obvious that the peak of red curve shifts two minor units towards right. Also, the slope of red curves after the peak point is greater than the other two curves. Due to the peak point of absorbance curve representing the properties of AuNPs, there are two probabilities: the size of AuNPs in the AuNPs NMP solution increases. Since the AuNPs is standard and stable by the introduction of the product, their size would not change. Thus, the only logical possibility is slight aggregating. Based on the shape and peak point of green curve is the same as the ones of blue curve, evaporating does not affect the AuNPs.

**Ionic Conductivity:**
At room temperature, GPE is placed between two steel chips as two blocking cells to measure the impedance. In high frequency range (100000Hz - 10000Hz), the Nyquist plots act as a vertical line; and the effect of the imaginary part of impedance can be neglected. Then, after extending the vertical lines for both GPE with AuNPs and GPE without AuNPs, there are two intersecting points that meet the Z-Re-axies. At the intersecting points, the value of real impedance can be written as the internal resistance. Also, the ionic conductivity (σ) is calculated by the Equation (1).

\[
\sigma = \frac{l}{RA}
\]  
(1)
The value of each term for both GPE with AuNPs and GPE without AuNPs lists in Table 1. According to the data, the ionic conductivity of GPE with AuNPs (0.96E-3 S/cm) is much greater than the ionic conductivity of GPE without AuNPs (1.18E-4 S/cm). Because of AuNPs, shorter lithium ions’ route in GPEs provides higher efficacy of the cell during the charging and discharging process.

![Figure 5: Comparison of the impedance for steel/GPE/steel with AuNPs and without AuNPs at high frequency](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>t (mm)</th>
<th>R (ohm)</th>
<th>A (cm²)</th>
<th>σ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPE with AuNPs</td>
<td>0.31</td>
<td>17</td>
<td>1.89 cm²/2</td>
<td>0.96 E-3</td>
</tr>
<tr>
<td>GPE without AuNPs</td>
<td>0.35</td>
<td>157</td>
<td>1.89 cm²/2</td>
<td>1.18 E-4</td>
</tr>
</tbody>
</table>

Table 1: Values of each term in calculating ionic conductivity

**Interfacial properties:**
As Figure 7 showing, the Nyquist Plots for both cell with AuNPs and cell without AuNPs consist of semicircles. At high frequency and low frequency, the capacitive contribution is neglected; and it acts as pure resistance. Meanwhile, at the medium frequency, the semicircle reflects the most capacitive contribution. By assuming that semicircle is associated with parallel combination of interfacial resistance and the constant-phase element (CPE), the system of can be described using the equivalent circuit in Figure 6.

![Figure 6: Equivalent circuit of Lithium-ion polymer cell](image)

The solution resistance indicates the pure resistance at high frequency that also relates to bulk resistance of the polymer electrolyte; and the value of R, locates in the left starting points in the Nyquist plots. R, of the cell without AuNPs (200 Ohms) is approximately 100 times the cell with AuNPs (2 Ohms), which proves GPE with AuNPs has excellent conductivity comparing with the normal one. At low frequency, the value of the right ending points in the Nyquist plots is sum of charge-transfer resistance and solution resistance. According to Nyquist plots, R, for cell without AuNPs is around 7300 Ohms; and R, for cell with AuNPs is around 145 Ohms. The double-layer capacitance can be calculated by Equation (2) and Equation (3).

\[ f_m = \frac{f_1 + f_2}{2} = \frac{1.0E5Hz + 0.1Hz}{2} = 50,000Hz \]  

\[ C_{DL} = \frac{2\pi}{f_m Z_{int,m}} \]

![Figure 7 a) Nyquist plots obtained for LIPB with AuNPs for 1 month at room temperature, b) Nyquist plots obtained for LIPB with AuNPs for 1 month at room temperature](image)

In this case, estimated \( C_{DL} \) for cell without AuNPs (46.5nF) is significantly smaller than estimated \( C_{DL} \) for AuNPs (2.28μF). Higher capacitance indicates more energy can be stored in each individual cell. In the parallel combination of double-layer capacitance and charge-transfer resistance, the lithium-ion polymer cell with AuNPs with lower internal resistance and higher capacitance in a certain size improves the performance of the whole battery.
From the Nyquist plots, the diameter of each semicircle reduces and then extends over time. In the first few days, it takes time for LiPF6 flooding the half amorphous structure; also the cell is not fully discharged. Between day 4 and day 7, there exists the smallest diameter for both cases. In the end of the month, the diameter reaches the largest value due to small amount of PVdF is dried. In day 30, the curve of cells with AuNPs is not as smooth as other. As previously mentioned, aggregating is one of the issues in this work; so in long term it will infinitesimally affect the performance of the cell.

CONCLUSION
The gel polymer electrolyte is a membrane synthesized by trapping EC and PC in PVdF and 1-methyl-2-pyrrolidinone solutions. Besides applying phase transfer method, AuNPs are added in gel polymer electrolyte as fillers, which enhance the ionic conductivity and the performance of the whole battery. After applying the AuNPs, the ionic conductivity of gel polymer electrolyte increased 10 times the general gel polymer electrolyte. As part of lithium-ion polymer cell, the gel polymer electrolyte with AuNPs lead to higher capacitance and lower internal resistance. Even if there exist aggregating, the amount is so small that it can be neglected.

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REFERENCES


