

Application of Polydopamine Doped Gel Electrolyte to Improve Lithium-Ion Battery Performance

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1. Introduction

The rapidly and globally increasing demand for energy results in challenges concerning not only the conversion but also the storage of electrical energy. The currently most common battery systems are based on the Li-ion technology. This technology was proposed by M. S. Whittingham in 1976, commercialized by SONY in 1990, and represents the best investigated and, due to its uniquely high-power density, most popular battery system today. However, for applications related to the Internet of Things (IoT), such as aRFID tags, sensors, smart clothes, or smart packaging, and flexible Organic Light emitting diode (OLED) the Li-ion technology reaches its limits. The demands for such thin-film applications clearly differ from conventional batteries (e.g., consumer electronics or electromobility). Vital requirements are flexibility, absence of toxic and harmful metals, the production from abundant and, ideally, renewable resources, rapid charging, excellent cycle life, and efficient processing using roll-to-roll or similar processing techniques (Muench et al., 2016).

According to Kong et al (2012) Carbonized Polydopamine (C-PDA) coating buffers the large volume change of SnO₂ clusters during the discharge–charge process and prevents their aggregation, which is confirmed by the well retained morphology after the cycling test. The C-PDA coating also acts as a conducting medium to ensure smooth lithium insertion/extraction because of the high electrical conductivity of C-PDA and the bridge-like C-PDA connections among the small C-PDA/SnO₂ clusters. This mechanism has been proven to improve the performance of the SnO₂-based lithium ion battery anodes.

2. Significance

Application of gel polymer electrolytes (GPE) in lithium-ion polymer batteries can address many shortcomings associated with liquid electrolyte lithium-ion batteries. There has been a significant increase with concerns regarding the issues associated with such batteries. Use of flammable organic solvents as electrolyte, formation of lithium dendrites, and large volume change due to poor structural stability are among the main concerns associated with Li-ion batteries. Use of gel polymer electrolytes (GPEs) has addressed some concerns regarding leakage of liquid electrolytes and the resultant fire hazards (Zhang, Chen & Montazami, 2015)

Gel polymer electrolytes, which are prepared by gelling liquid electrolytes with polymer matrices, have advantages over both liquid electrolyte and ceramic (glass) electrolytes. Porous gel polymer electrolytes (PGPEs) combine electrolyte and separator as an integrated membrane. Compared with liquid electrolytes, polymer electrolytes can effectively prevent electrolyte leakage and reduce the firing hazard, which leads to the high safety of batteries. Meanwhile, porous polymer electrolytes can provide high ionic conductivity, good processability, a wide electrochemical operating window, and good thermal stability (Zhang, Sun, Huang, Chen & Wang, 2014).

3. Methodology

3.1. Material

First PDA is deposited onto an oxidized silicon wafer and then carbonized. Copper foil single-side coated by 0.1 mm of composite PDA anode and aluminum foil single-side coated by 0.1 mm of lithium manganese oxide (LiMn_2O_4) cathode. N-Methyl-2-pyrrolidone (NMP), ethylene carbonate (EC), propylene carbonate (PC), lithium hexafluorophosphate (LiPF_6), polyvinylidene fluoride (PVdF), and 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate (EMI-Tf) will be used for membrane synthesis process. EMI-Tf is selected because of its high ionic conductivity ($10\text{--}2\text{ S/cm}$) and wide electrochemical window. LiPF_6 is selected as the lithium salt due to its high conductivity in carbonates solvent mixtures, also due to its ability to prevent aluminum corrosion at the cathode aluminum current collector by forming a passivation layer. (Zhang, Chen & Montazami, 2015).

3.2. Electrolyte Preparation

One M of LiPF_6 is dissolved in a solvent consisting of EC, PC and EMI-Tf at different ratios then will be used as electrolyte solutions. EC, PC and EMI-Tf are mixed at desired ratios (Table 1) and stirred for at least 2 h; lithium hexafluorophosphate is added to the solvent under an inert gas environment to achieve 1 M concentration, and stirred for 24 h (Zhang, Chen & Montazami, 2015).

Compound	GPE Composition (vol%)							
EMI-Tf	0%	25%	30%	40%	50%	60%	75%	100%
EC	50%	37.5%	35%	30%	25%	20%	12.5%	0%
PC	50%	37.5%	35%	30%	25%	20%	12.5%	0%

Table 1. Gel polymer electrolyte (GPE) composition

3.3. Synthesis and Activation of Membrane

The first step of the membrane synthesis is by preparing a carbonate ester mixture. A 1:1 weight ratio mixture of EC and PC was heated to 80 °C to achieve complete dissolution. The resultant clear carbonate ester solution is mixed with PVdF and 1-Methyl-2-pyrrolidone at 10:4:11 weight ratio. The mixture is then heated to 110 °C and stirred on a magnetic stirrer until a clear solution was obtained with a relatively high viscosity. The solution is then casted on a glass template and dried under vacuum at 80 °C for 2 h to form membranes. The membranes are then soaked in a 10% ethanol aqueous solution overnight. Pale yellow membranes with 50 μm thickness are obtained and cut into 22 mm $\times$ 22 mm squares and stored under ambient conditions. Membranes are then activated by full exposure (immersion) to electrolyte solution for 24 h.

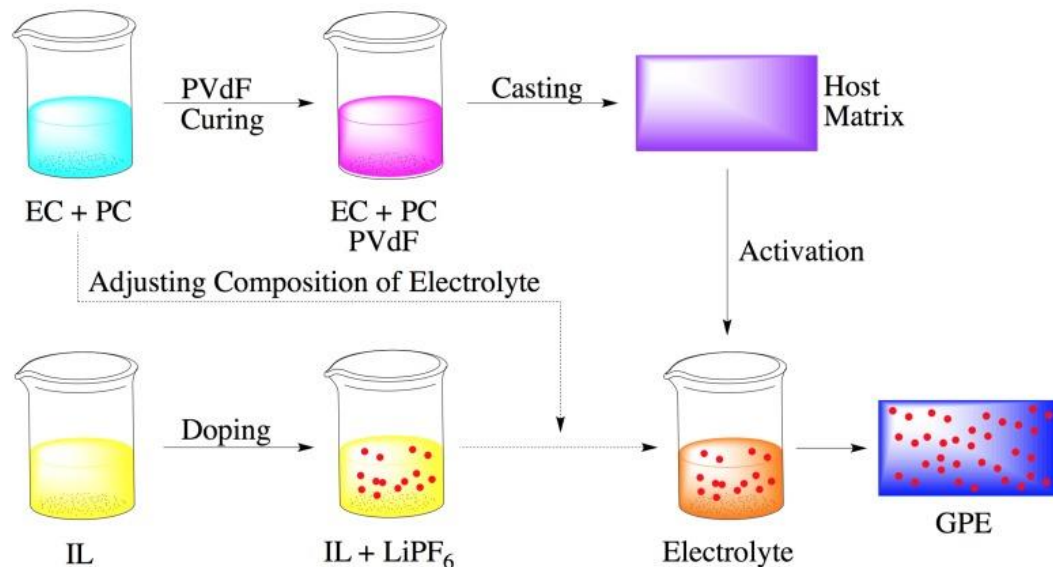


Fig.1. Process for fabrication and activation of GPEs scheme

3.4. Cell Assembly

The current collector will be obtained by casting anode material of polydopamine on the surface of copper foil. The cathode material of LiMn_2O_4 is casted on the surface of aluminum foil as another current collector. Gel polymer electrolytes will be located in between the cathode and anode. The dimensions of cathode and anode are exactly 20 mm $\times$ 20 mm; but GPE film is larger than cathode and anode so the cell would not be shorted. The surface of protection cover that faces inside of the cell is adhesive, which helped airtight enclosure of the whole system.

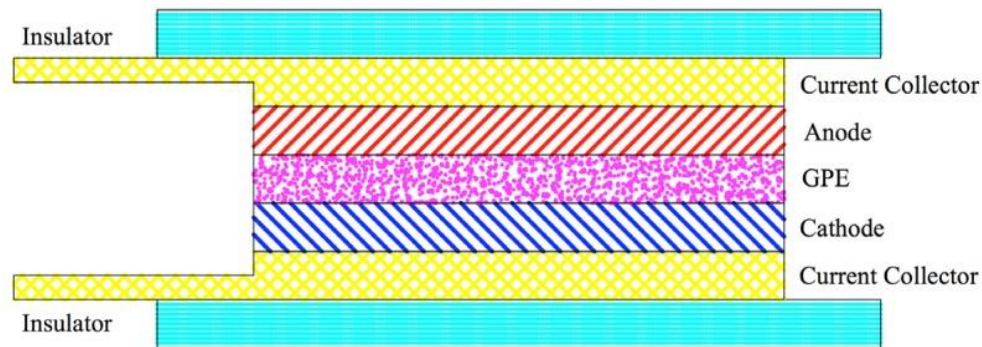


Fig.2. Cell structure scheme.

4. Thermodynamics Background of System

Solubility parameters are often used in industry to predict compatibility of polymers, chemical resistance, swelling of cured elastomers by solvents, permeation rates of solvents, and even to characterize the surfaces of pigments, fibers, and fillers (Grulke, 1999). The Flory–Huggins solution theory uses χ to determine whether two polymers (A and B) will be miscible

$$\chi_{AB} = (V_{ref}(\delta_A - \delta_B)^2)/RT \dots \dots \dots (1)$$

Where:

χ_{AB} is Flory–Huggins interaction parameter

V_{ref} is an appropriately chosen ‘reference volume’, often taken to be 100 cm³/mol

δ is solubility parameter of species i

And R is the gas constant

The solubility of a given polymer in various solvents is largely determined by its chemical structure. Polymers will dissolve in solvents whose solubility parameters are not too different from their own. This principle has become known as ‘like dissolves like’, and, as a general rule, structural similarity favors solubility. Dissolution of an amorphous polymer in a solvent is governed by the free energy of mixing (Miller-Chou & Koenig, 2003).

$$\Delta G_m = \Delta H_m - T\Delta S_m \dots \dots \dots (2)$$

Where

ΔG_m is the Gibbs free energy change on mixing,

ΔH_m is the change of enthalpy upon mixing

T is the absolute temperature, and

ΔS_m is the change of entropy of mixing

Hildebrand and Scatchard proposed that the enthalpy of mixing is given by:

$$\Delta H_m = V_{mix}((\Delta E_1^V/V_1)^{\frac{1}{2}} - (\Delta E_2^V/V_2)^{\frac{1}{2}})^2 \phi_1 \phi_2 \dots \dots \dots (3)$$

Where

V_{mix} is the volume of the mixture

ΔE_i^V is the energy of vaporization of species i

V_i is the molar volume of species i

and ϕ_i is the volume fraction of i in the mixture.

The cohesive energy, E; of a material is the increase in the internal energy per mole of the material if all of the intermolecular forces are eliminated. The cohesive energy density (CED) is the energy required to break all intermolecular physical links in a unit volume of the material

$$CED = \frac{E}{V} = (\Delta H_{vap} - RT)/V \dots \dots \dots (4)$$

where ΔH_{vap} is the enthalpy of vaporization

The Hildebrand solubility parameter is defined as the square root of the cohesive energy density:

$$\delta = (E/V)^{1/2} \dots \dots \dots (5)$$

Eq. (3) can be rewritten to give the heat of mixing per unit volume for a binary mixture:

$$\Delta H_m/V = (\delta_1 - \delta_2)^2 \phi_1 \phi_2 \dots \dots \dots (6)$$

Hansen accounted for molecular interactions and developed solubility parameters based on three specific interactions. The first and most general type of interaction is the ‘non-polar’, also termed dispersive interactions, or forces. Polar cohesive forces, the second type of interaction, are produced by permanent dipole–dipole interactions. The third major interaction is hydrogen bonding. Hydrogen bonding is a molecular interaction and resembles the polar interactions.

Hansen proposed, the cohesive energy has three components, corresponding to the three types of interactions:

$$E = E_D + E_P + E_H \dots \dots \dots (7)$$

Dividing the cohesive energy by the molar volume gives the square of the Hildebrand solubility parameter as the sum of the squares of the Hansen dispersion (D), polar (P), and hydrogen bonding (H) components:

$$E/V = E_D/V + E_P/V + E_H/V \dots \dots \dots (8)$$

$$\delta_2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \dots \dots \dots (9)$$

5. Result Measurement

5.1. Ionic Conductivity

According to Zhang et al. (2015) AC Impedance spectroscopy will be used to study ion conductivity of GPEs. GPEs doped with electrolytes of different composition were secured between two steel disks and studied at a high frequency range (10–100 kHz). Ionic conductivity of GPEs can be calculated using internal resistance, thickness and surface area of the GPEs. The ionic conductivity σ for each GPE sample was calculated using Equation (10)

$$\sigma = \frac{t}{RA} \dots \dots (10)$$

where t is the thickness of each sample, R is the internal resistance and A is the surface area.

5.2. Battery Performance

The performance of lithium-ion polymer batteries *containing GPE of different ionic liquid conten* can be evaluated by Galvan static charging and discharging. Each cycle includes constant current (0.5 A) discharging followed by an 8 min rest period, then constant current and constant voltage charging. The average rest voltages and discharge capacity of Li-ion polymer batteries as function of GPE composition will also be conducted to obtain the correlation between concentration and performance (Zhang, Chen & Montazami, 2015).

6. Conclusion

In summary, C-PDA coatings has a fairly ordered multilayered structure doped with heteroatoms, rendering it high electrical conductivities. This feature, coupled with the good thickness controllability and the strong affinity of PDA to a rich variety of solid surfaces, make C-PDA a more attractive coating material for improving lithium-ion battery compared to other materials such as graphene. Also, the coating mechanism is less complicated compared to the other materials. Those advantages make C-PDA coatings a suitable battery performance improving process for general energy storage or for flexible wearable electronic device.

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