Preparation and properties of UHMWPE microporous membrane for lithium ion battery diaphragm

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Abstract. Based on the principle of heat-induced phase separation (TIPS), the ultrahigh molecular weight polyethylene (UHMWPE) microporous membrane was prepared. The effects of material formula and preparation process on the structure and properties of UHMWPE microporous membrane and the internal relationship between the process parameters and the performance of microporous membrane were studied. The forming process of microporous membrane was optimized and the UHMWPE microporous membranes with different properties were prepared and assembled into the half-battery and the full battery. The key electrochemical properties of lithium ion batteries, such as ion conductivity and cycle performance, were tested. The properties of lithium ion battery was explored. Results shown that the UHMWPE microporous membrane met the requirements of power lithium ion battery.

1. Introduction

UHMWPE microporous membrane has excellent mechanical properties and chemical stability, it has big potential application prospect in the field of lithium ion batteries. However, The preparation process of microporous membrane based on the TIPS of UHMWPE is relatively complex, and the research on the process factors affecting microporous membrane structure is less. Therefore, in this paper, based on the principle of thermal induced phase separation (TIPS) the forming technique of preparation of UHMWPE microporous membrane system was studied, and the influence of average molecular weight of UHMWPE, material proportion and preparation technology on the properties of UHMWPE structure was studied. The UHMWPE change rule of crystalline morphology in the process of UHMWPE microporous membrane preparation was explored, the relation between process parameters and product performance was studied, the preparation technology of UHMWPE microporous membrane and the associated properties that UHMWPE microporous membrane and the performance of lithium ion battery using properties such as ionic conductivity and cycle performance were also researched.

Lithium ion battery has high working voltage, large energy density, no memory effect, long cycle life and green environmental protection, and many other advantages. In recent years, it has become one
of research hotspots in the field of new energy materials. Lithium ion batteries are used in aerospace, communications, medical, transportation, and many other areas of electronics. Lithium ion battery is gradually replace the traditional lead acid and nickel metal hydride batteries. It plays an important role\(^\text{[4-5]}\) in car instead of petrochemical energy as a driving force.

2. Experimental

2.1 Materials
UHMWPE number average molecular weight are: 2.0×10^5 ,5.0×10^5 ,8.0×10^5 ,1.1×10^6 ,1.3×10^6 ,2.0×10^6 , purchase from Mitsui chemicals company in Japan; Liquid paraffin oil) 70#, kinematic viscosity was 70mm2/s (40°C), flash point: 200 °C or higher. Bought in hangzhou petrochemical co., LTD; Antioxidant 1010 hindered phenols, bought in ciba company.

2.2 Preparation of UHMWPE Membrane
Put the UHMWPE (powder), antioxidants, liquid paraffin oil (LP) in mechanical premixed according to certain proportion within the agitator, Then after the premixed material was added to the synthetic twin screw extruder (L/D = 60:1, φm = 40, Nanjing KeYa company) , Material in the extruder melt mixing, plasticizing completely, and then after T die stretch film to the rapid cooling roller, By controlling the quenching of roller temperature, producing UHMWPE slabs under different cooling rate; Then with adjustable stretch ratio of homemade tensile testing machine (8.0 x8.0 maximum tensile rate), the UHMWPE thick slices respectively in different stretching temperature, into the ventilation conditions, for different ratio of tensile. Then with a homemade extraction machine stretch film to extraction respectively, formed with microporous stretch film. Finally, with the heat setting machine will microporous stretch film for heat setting, get the UHMWPE microporous membrane.

3. Results and Discussion

3.1 The effect of UHMWPE formula and diluent on the microporous membrane structure and performance
This study selects the liquid paraffin oil as diluent of UHMWPE. The formula of UHMWPE and diluent are the important factors which affect the structure morphology and properties of lithium ion battery using UHMWPE microporous membrane. Only at high temperatures UHMWPE and liquid paraffin can form the thermodynamics single-phase. This study was carried out at melt mixing experiment with different UHMWPE mass fraction (10%, 20%, 30%, 10%, 20%) , When the UHMWPE mass percent concentration is 10% and 20%, The melt strength of extruded UHMWPE thick sheets is lower. However, if the UHMWPE mass percent concentration is too high, the UHMWPE is difficult to disperse in the UHMWPE-diluent system, the mixing effect is poor, and the extruded sheet surface is rough. Figure 2 is the microstructure of UHMWPE microporous membrane prepared at UHMWPE mass fraction of 30%, 40%, 50%.. When UHMWPE mass percent concentration was 30%, pore diameter distribution is uniform and permeability is good. With the increment of UHMWPE mass fraction, the amount and the size of the pore gradually reduced. When UHMWPE mass fraction increased to 50%, microporous basically is closed. This is because, with the increasing of mass fraction UHMWPE the interaction between molecules enhanced and the mutual entanglement degree of UHMWPE macromolecular chain increased, therefore the tight interlaced
network formed. Experiments show that when UHMWPE mass fraction is 30%, the aperture size of UHMWPE microporous membrane is uniform, porosity is moderate.

![Fig.1 The surface morphology of the UHMWPE microporous membrane at different ratios between UHMWPE and Oil: (a) 20% (b) 30% (c) 40%.

3.2 The effect of stretching temperature on the microporous membrane morphology and porosity

The porosity of Lithium ion battery with microporous membrane are the key indicators of UHMWPE microporous membrane, it directly influence the battery capacity of the lithium-ion batteries and its safety. High porosity, can accommodate more electrolyte, upgrade the capacity of the battery.

Under the condition of the UHMWPE mass fraction of 20%, with stretching ratio 6x6 and stretching speed 10 mm/s, at 70℃, 90℃, 110℃ and 130℃ respectively, UHMWPE thick slices were stretched.

Figure 5 is the micro topography of UHMWPE microporous membrane under different tensile temperature. Experiments show that the tensile temperature is lower than 70 ℃, UHMWPE slabs stretching is difficult, stretch film is easy to break. When the tensile temperature reaches the fastest crystallization temperature 110℃, It is good for stretching, under this temperature, the membrane pore size distribution is uniform, moderate porosity was 42%. However, when the tensile temperature is much higher than the fastest crystallization temperature, the porosity is low. Therefore, at 90-110℃ stretching temperature with 6x6 longitudinal transverse stretching ratio, good mesh structure of the microporous membrane was obtained. Figure 6 is the relationship of the microporous membrane pore ratio and stretching temperature.

![Fig.2 Morphology of UHMWPE films with different stretching temperature](image-url)
3.3 The influence of UHMWPE microporous membrane on ionic conductivity of Li ion battery
The ionic conductivity of UHMWPE microporous membrane affects the discharge characteristics and capacity characteristics of lithium ion batteries. It is an important index to measure the electrical properties of UHMWPE microporous membranes. The porosity of UHMWPE microporous membrane has an important influence on the ionic conductivity of Li ion battery. Samples of UHMWPE microporous membranes with porosities of 33%, 36%, 38% and 42% were assembled into button half cells and tested for ionic conductivity. Fig. 7 is the relationship between the porosity of the UHMWPE microporous membrane and the ionic conductivity. As can be seen from the diagram, the ionic conductivity increases with the increase of porosity of UHMWPE microporous membrane, because as the porosity of UHMWPE microporous membrane increasing, the capacity of microporous membrane to absorb electrolyte increases.

4. Conclusion
(1) using UHMWPE - liquid paraffin oil system produce UHMWPE microporous membrane, when UHMWPE mass percent concentration is 30%, the UHMWPE has good dispersion in the system of microporous membrane and the pore aperture size is moderate, pore size distribution is uniform. The microporous membrane can meet the performance requirements of the lithium ion battery.
(2) The drawing process have important influence on the microstructure and physical properties of UHMWPE microporous membrane. When the longitudinal transverse stretching ratio is 5x5, stretching temperature is 90-110 ℃, the microporous membrane has good mesh structure, pore size distribution is uniform, the connectivity is good, porosity is moderate, microporous membrane thickness is uniform, which can basically meet the performance requirements of lithium ion battery.
(3) when the porosity is 38% - 38%, Lithium ion battery has good ionic conductivity.

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