Preparation and Characterization of a Novel Polyvinyl Formal Based Gel Polymer Electrolyte
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Safety becomes particularly important for the application of lithium-ion batteries as the power source for vehicles and also as energy storage device for distributed generation. Gel polymer electrolytes (GPEs) have recently received much attention owing to their high ionic conductivity at ambient temperature and absence of risk for leakage of electrolyte [1]. Previous studies of GPEs have proposed numerous systems based upon polymers such as polyethylene oxide (PEO) [2], polyacrylonitrile (PAN) [3], polymethyl methacrylate (PMMA) [4] and polyvinylidene fluoride (PVDF) [5] etc. The works are mainly focused on the exploration of polymer electrolyte with further improved performance in ionic conductivity, chemical-, thermal- and electrochemical- stability, and mechanical strength to realize its wide application in lithium-ion batteries. Polyvinyl acetal and its derivatives have been widely noted for their advantages such as excellent thin-film forming ability, good heat- and water-resistance and relatively stable chemical structure. Polyvinyl acetal based gel polymer electrolytes have recently drawn increased attention. In the paper, novel PVFM based GPEs are developed using an initiator-free thermal polymerization method. Novel polyvinyl formal (PVFM) based gel polymer electrolytes (GPEs) are developed using an initiator-free thermal polymerization method [6]. The polymerization mechanism during the cross-linking process is investigated by means of Fourier transform infrared (FTIR) spectroscopy measurements. The effect of PVFM on the thermal stability of electrolytes was studied using differential scanning calorimetry (DSC); the components of evolved gases from GPE and liquid electrolyte during the heating process were comparatively analyzed by thermogravimetry-infrared spectrum/mass spectrometry (TA-FTIR/MS). With the prepared GPEs (containing 2 to 5 wt % PVFM), Li polymer batteries with LiPF6 as the cathode are assembled, and the electrochemical properties such as interfacial impedance, electrochemical stability window and cycling performance are evaluated.

It is found that homogenous mixture solutions of PVFM and the liquid electrolyte 1M LiPF6(EC: DMC = 3:7 (V/V)) are successfully turned into a self-standing gel after a thermal treatment without employing any thermal initiator. The as-prepared GPEs shows better thermal stability compared with the liquid electrolyte (as shown in Fig.1). The macroscopic physical network formed by PVFM after polymerization can prevent the organic solvents from evaporating at high temperatures effectively, and reduce HF content in electrolytes as well.

The sample containing 4 % of PVFM exhibits an acceptable conductivity of 8.82 mS•cm⁻¹ at 25 °C. The FTIR results indicate that the polymerization occurs through the interaction between C-O-C bonds, which are arisen from the breaking of ether linkage bonds in PVFM, and the strong Lewis acid PF5 generated by the slight decomposition of the LiPF6 salt. Cyclic voltammetric (CV) curves reveal that the electrochemical stability window of PVFM-based GPE is 1.5 to 5 V vs. Li/ Li+ and wider than that for the corresponding liquid electrolyte which is 1.8 to 4.5 V.

Fig.1 TGA-DSC analysis of the PVFM, liquid electrolyte and the GPE under argon atmosphere at a scanning rate of 10°C/min

Fig.2 Conductivities and the fitted results of the liquid electrolyte and gel polymer electrolytes; Note: The liquid electrolyte used is 1.0 M LiPF6 in EC: DMC=3:7 (in vol).

Fig.3 Cyclic voltammetry of the GPE on stainless steel at a scan rate of 5 mV•s⁻¹.

The discharge capacity of the polymer Li/LiFePO4 battery is 145 mAhg⁻¹ over a voltage range of 2.5-4.25 V at 1/10 C rate after 50 cycles with a small capacity fade. Overall, the novel PVFM based GPE is a promising electrolyte to achieve enhanced thermal stability and improved safety.

Reference:

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