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We have fabricated a poly(vinylidene fluoride)(PVdF)/poly(ethylene glycol diacrylate)(PEGDA) blend membranes incorporated with liquid electrolyte for Li rechargeable batteries. We developed PVdF/PEGDA/Nafion blend for proton membrane fuel cells (PEMFC). UV or thermally cured PEGDA improved cycle performance of Li cells at high temperature by increasing thermal stability of PVdF and enhanced proton conductivity of Nafion/PVdF blend membrane by increased water retention. The Li cell capacity of PVdF/PEGDA reached 120 mAh/g, and ternary blend membrane for PEMFC showed maximum power of 350 mW/cm^2.

Keywords PEGEA; PVdF blend membrane; Li-batteries; Fuel cell

INTRODUCTION

PVdF is the most popular solid polymer electrolyte in electrochemical society, because of their mechanical properties and electrochemical stability in the several redox conditions. PVdF is not stable enough to

apply to Li-cell at high temperature and too hydrophobic to be applied as a proton exchange membranes. Thus, we fabricated PVdF blend with PEGDA by UV curing for rechargeable Li batteries [1] and by thermal curing for PEMFC [2]. Interlocking introduced by PEGDA network structure enhanced thermal stability of PVdF. Hydrophilic ethylene oxide unit of PEGDA increased water retention, which resulted in increased proton conductivity of PVdF/Nafion blend membrane.

EXPERIMENTAL

UV cured membrane

EGDA oligomer (Aldrich, 14 EGDA: d=1.120, Mn≒740) was mixed with PVdF-HFP copolymer(Atochem Kynar 761®)/Nafion(E. I. DuPont EW 1100) and electrolyte solution consisting of 1M $LiPF_6$ as lithium salt in ethylene carbonate(EC), dimethyl carbonate(DMC), and ethyl methyl carbonate (EMC) for 3 hours. Then initiator and accelerator were added prior to UV irradiation. A cycle performance was obtained using $LiCoO_2$ a cathode and a carbon anode at room temperature.

Thermally cured membrane

PVdF (Elf Atochem, Kynar 2801) and Nafion were dissolved in organic solvents and ultrasonifically mixed and then the blend solution was mechanically mixed with PEGDA oligomer containing initiator and thermally cured during casting film. 5-cm^2 single cell was operated using high purity hydrogen to cathode and oxygen to anode at 80 °C and 1 atm.

RESULTS AND DISCUSSION

Microporous PVdF gel polymer electrolyte has good Li conductivity and good mechanical properties. But it could be partially dissolved out in carbonate solvent during Li cell operated at high temperature. But

PVdF blend cured with PEGDA improved thermal stability by forming 3 dimensional network structures.

Fig. 1 shows cycle performances of PVdF/PEGDA binary blend membranes at various blend ratios. Binary system of PVdF/PEGDA performed much batter cycleability at high temperature than conventional UV cured PEGDA system.

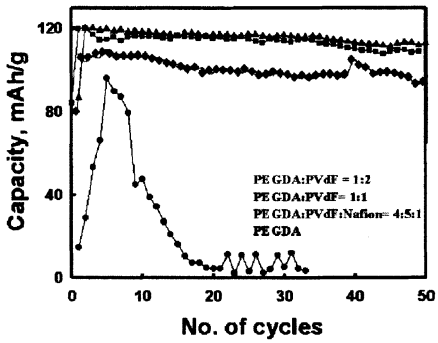

FIGURE 1. Cycle life of $LiCoO_2$/C cell at 80 °C.

Fig. 2 shows room temperature proton conductivity of PVdF/Nafion blend membranes as a function of Nafion content. The proton conductivity of pure Nafion 117 reaches about 0.081 S/cm. PVdF/Nafion blend usually shows phase seperation but a misible blend of Nafion with PVdF was obtained above 70 wt% of Nafion. But binary blend membrane showd much lower proton conductivity than pure Nafion. Hydrophobic PVdF backbone might strongly prevent ionomer component from absorbing water molecules, resulting in poor proton conductivity. However the water retention was improved by addition of PEGDA network into blend film. N/P/G =7/1/2 blends showed comparable conductivity with pure Nafion membrane.

Fig.3 shows single cell performances using different membranes. All polarization curves are very similar at temperature of Anode/Cell/Anode=95/75/85 °C and pressure of Anode/Cathode=30/30 psig. A ternary blend of Nafion/PVdF/PEGDA (7/1/2, wt/wt) and 40

wt% Pt/C catalyst (0.4 mg/cm^2 Pt loading) showed maximum power of 350 mW/cm^2 at 75 °C and atmospheric pressure

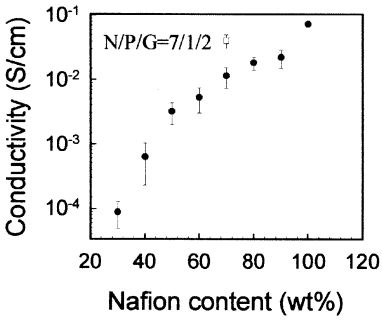

FIGURE 2. Proton conductivity of blend membrane.

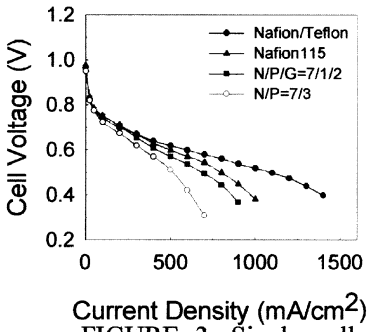

FIGURE 3. Single cell polarization curves..

CONCLUSIONS

UV-Cured PEGDA/PVdF blend electrolytes were prepared to improve battery performance at high temperature. Water retention and room temperature proton conductivity were improved by incorporation of hydrophilic PEGDA to Nafion/PVdF blend. Max. power density for N/P/G=7/1/2 blend reached ca. 350 mW/cm2

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