

PVdF-HFP Gel Electrolytes with an Asymmetric Ammonium Salt for Electric Double Layer Capacitors

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An electric double layer capacitor (EDLC) is a promising energy storage device that can assist chemical battery systems in load leveling and high-rate charging-discharging. We have proposed novel, non-aqueous EDLC systems composed of activated carbon fiber cloth electrodes and organic gel electrolytes with tetraethylammonium (TEA) BF₄ salt (1-4). Our gel electrolytes have consisted of a polymer matrix such as PEO-PMMA (1,2), PAN (3), or PVdF (4) and typically PC as a plasticizer. TEABF₄ has generally been regarded as a suitable salt for organic gel electrolyte systems to provide high capacitance and good electrochemical stability. Recently, we applied an asymmetric ammonium salt, triethylmethyl (TEMA) BF₄, to gel electrolytes based on PVdF with PC (5). It was found that EDLCs with the PVdF/PC/TEMABF₄ systems provided a higher capacitance than those with the PVdF/PC/TEABF₄ systems.

We report herein the performance of gel-type EDLCs with poly-(fluorovinylidene-hexafluoropropylene) (PVdF-HFP) containing TEMABF₄ and PC. PVdF-HFP has been known to have a unique property; an amorphous HFP domain can keep a large amount of plasticizer such as PC while a VdF domain enhances the mechanical strength of gels. Thus the combination of TEMABF₄ and PVdF-HFP/PC is expected to provide superior EDLC performances.

The PVdF-HFP gel systems were prepared by mixing PVdF-HFP and TEMABF₄ (or TEABF₄) in PC, followed by evaporation of the PC solvent in a vacuum oven. All the films were prepared to have an identical 3/1 weight ratio of electrolytic salt and PC to PVdF-HFP. The film composition is represented by molar quantity based on the amount of electrolytic salt per PC volume contained in the films. A test cell for EDLCs was constructed with the gel film and two electrodes made of an activated carbon fiber cloth whose specific surface area is about $1.9 \times 10^3 \text{ m}^2 \text{ g}^{-1}$.

The PVdF-HFP/PC/TEMABF₄ electrolytes show a higher conductivity (above 7 mS cm^{-1} at 298 K) than the PVdF-HFP/PC/TEABF₄ electrolytes. The capacitance of EDLCs with the TEMABF₄ gels is higher than that with the TEABF₄ gels. The difference in capacitance should

be ascribed to differences in the size of ammonium cations ($\text{TEMA}^+ < \text{TEA}^+$) and in the ionic conductivity of gel electrolytes. The former affects the availability of pores distributed over the activated carbon electrode surface while the latter governs the magnitude of IR loss during charge-discharge cycling. Judging from our data, a concentration above 1.5 mol dm^{-3} should be desirable to provide good capacitance for practical use. In such a concentration region, the gel capacitors show a high efficiency (more than 98.0%) for 1.0-2.5 V.

Based on *ac* impedance measurements, in the high concentration region over 1.5 mol dm^{-3} the TEMABF₄ gel systems have a lower resistance of the gel electrolyte bulk itself and also a lower interface resistance between the electrode and the gel electrolytes than the corresponding TEABF₄ systems. Thus the TEMA⁺ cation should have high-rate diffusion ability at the interface between the carbon electrode and the PVdF-HFP gel electrolytes even when its concentration is very high.

It should be noted that the EDLCs with the PVdF-HFP/PC/TEMABF₄ gels provide much higher capacitance (ca. 60 F g^{-1}) than the EDLCs with the PVdF-HFP/PC/TEABF₄ gels (ca. 25 F g^{-1}) with a relatively high rate current (e.g., 15 mA cm^{-2}). This should be ascribed to the lower resistance of the TEMABF₄ gel electrolyte bulk itself and also to the lower interface resistance between the electrode and the TEMABF₄ gel electrolytes as observed in the *ac* impedance measurements.

The present study suggests that TEMABF₄ is a suitable electrolytic salt for PVdF-HFP gel electrolytes applicable to EDLCs. It provides a high capacitance and efficiency as well as especially desirable interfacial properties such as the low diffusion resistance in its high concentration region.

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