

Nonaqueous proton conducting electrolytes and their application in supercapacitors

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Abstract

Our generation has to deal with increasing energy demands and the associated environmental concerns. To solve this issue, research activities are focused on the development of efficient technologies for energy storage, conversion and transport. Nowadays, various devices are available as electrochemical energy sources, i.e. batteries (Li-ion, Na-ion, alkaline, sulfur, etc.), supercapacitors (electrochemical double-layer capacitors, redox or hybrid systems), fuel and solar cells.

Supercapacitors are energy storage devices that can deliver high power during few seconds. Based on electrostatic adsorption of ions from an electrolyte onto porous carbon electrodes with large specific surface area ($1000\text{--}2000\text{ m}^2\text{ g}^{-1}$), EDLCs show high power density and can store more charge than conventional capacitors. However, EDLC energy density is far below than that of batteries and the energy density of EDLCs must be increased for broadening their range of applications. Recent studies focused mostly on the development of electrode materials to improve capacitance in supercapacitors, and often neglected another key material affecting electrical properties: the electrolyte.

An appropriate electrolyte can increase the energy density by increasing the cell voltage and expanding the working temperatures range. Despite of advantages of liquid electrolytes, use of semi-solid - rather than liquid - systems would be advantageous because many problems related to packing issues, corrosion, self-discharge or leakage currents could be solved. However, the key issue is to maintain a high ionic conductivity as well as a good contact at the electrolyte-electrode interface. This requirement is of particular importance for EDLCs, where high surface area carbons are used as active materials. One of the solutions proposed to tackle these issues is the combination of liquid and polymer electrolytes to form gel polymer electrolytes (GPEs). GPEs have several advantages that include processability and flexibility of polymer matrices, thus enabling good contact at the electrode / electrolyte interface.

In the present work, nonaqueous proton-conducting GPEs based on methacrylate matrix were considered here for application in solid-state type supercapacitors. Replacing water with organic solvents allows expanding the voltage and the operation temperature range of such electrolytes. Firstly, the preparation and physicochemical characterizations of GPE prepared from various components was achieved. The ionic conductivity as well as the proton transport mechanisms and thermal properties have been studied and characterized versus the electrolyte composition. The highest ionic conductivities at room temperature were obtained for GPE based on phosphoric acid ester (diphenyl phosphate), PC-DMF solvents mixture (7:3 ratio) and methacrylate copolymer based matrix ($3.1 \times 10^{-4} \text{ S cm}^{-1}$ for GPE with 15 wt. % of diphenyl phosphate). It was shown that for electrolytes based on phosphoric acid ester as a proton donor source (instead of phosphoric acid), the electrolyte ionic conductivity was an order of magnitude higher in the entire temperature range (-40-80 °C). The analysis of thermal properties shown GPE electrolytes stability in analyzed temperature working range and the only phase transition is glass transition at ~ -100 - -90 °C (depends on GPE composition).

Electrochemical supercapacitors cells using activated carbon as active materials and the prepared gel polymer electrolytes (with different GPE composition) were characterized at room temperature using cyclic voltammetry, galvanostatic charge-discharge cycle tests and impedance spectroscopy. The use of PC-DMF solvent mixture instead of pure PC allows to move from a conventional vehicle-type to a Grotthuss-type proton conducting mechanism, thus improving the ion accessibility in the porous carbon network. The use of phosphoric acid ester (instead of phosphoric acid) as proton donor led to an increase in the operation voltage window (up to 1.3 V). The resulting double layer capacitance of the microporous activated carbon was found to be as high as 120 F g^{-1} ; even more important, the supercapacitor utilizing non-aqueous proton-conducting gel polymer electrolyte was able to operate in a large temperature range (namely, from -40 to 80 °C). Finally, the electrochemical characterizations of a supercapacitor cell using activated carbon electrodes and the GPE electrolytes have been achieved in a large temperature range (from -40 °C to 80 °C).

GPE with diphenyl phosphate were consider as well as an electrolyte in a system where were multi-walled carbon nanotubes (MWCNT) enriched with polyoxometalates were used as active materials. The cyclic voltammetry performed at room temperature (22 ± 1 °C) for uncoated and coated MWCNT with three different hetropoly acids (HPA) show that such GPEs can be used instead of aqueous H_2SO_4 in electrochemical double layer capacitors (EDLC).

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