



Electrochemistry of ruthenium dioxide composite electrodes in diethylmethylammonium-triflate protic ionic liquid and its mixtures with acetonitrile



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ABSTRACT

Ruthenium dioxide electrodes store charge via faradaic reactions involving proton exchange with the electrolyte, thereby achieving very high specific capacitance values that make it a very interesting material for electrochemical capacitors. We demonstrated earlier that these faradaic reactions occur for RuO₂ in non-aqueous electrolytes based on protic ionic liquids, but the specific capacitance were limited due to the high degree of crystallinity of the material prepared in thin films by thermal decomposition. In order to increase the specific capacitance and to evaluate the impact of proton transport and transfer in high load electrodes, RuO₂ was prepared by a conventional sol-gel route and used as the active material in a composite electrode to evaluate its electrochemical response in the protic ionic liquid diethylmethylammonium-trifluoromethanesulfonate (DEMA-TfO). Cyclic voltammetry was carried out in the pure DEMA-TfO as well as in mixtures of the ionic liquid with acetonitrile. The results showed a significant impact of the electrolyte viscosity and conductivity at high potential scan rates and a limitation of the proton transfer rate at low scan rates. The specific capacitance can be improved at low scan rates by increasing temperature, reaching a value of 338 F/g at 120 °C with a 2 mV/s scan rate. This value is by far the highest reported for RuO₂ in a non-aqueous electrolyte.

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1. Introduction

Electrochemical capacitors are high power energy storage devices storing charge either by non-faradaic process (electrochemical double-layer capacitors, EDLC) or via redox transitions taking place on the surface and, to some extent, in the bulk of the electrode active material (pseudocapacitors).[1–5] Currently commercialised electrochemical capacitors are EDLC devices due to the lost cost high surface area carbons available, compatibility with non-aqueous electrolytes for high operating voltages, and excellent stability in the hundreds of thousands of cycles. EC are found in a plethora of applications where high power, intermittent, energy storage is required. These applications range from consumer electronics to electric and hybrid vehicles and their use is expected to play an important role in the powering of microsystems.[6]

The development of more advanced electrochemical capacitors is intimately linked to the development of electrolytes with

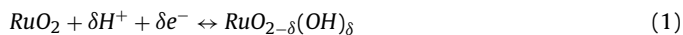
improved properties and that are designed to fit specifically to a given electrode material. This is also true for other types of energy storage and conversion devices. Ionic liquids make very attractive electrolytes due to their wide range of liquid state, very low vapor pressure and large electrochemical window of stability. It is widely recognized that ionic liquids (ILs) could play a first role in EC development by overcoming the shortcomings of traditional solvent-based or aqueous-based electrolytes. For example, ILs can be used to provide EC with a broad operating temperature, wider potential window of operation, and better prevention of current collector corrosion.[7–9] As EDLC rely on electrostatics for charge storage, a broad selection of ionic liquids has been shown to work as the electrolyte with carbon electrode materials, although it is now demonstrated that the size and structure of the ions play an important role in the charge storage mechanisms.[10,11] In the case of pseudocapacitors where faradaic charge transfer is involved, the nature of the ionic liquid also plays a determinant role in the type of mechanism leading to charge storage since these reactions require the reaction of species found on the structure of the electrolyte components. Metal oxides such as RuO₂ are excellent active materials for pseudocapacitors, but their redox reactions are based on an exchange of protons (or hydroxyls) with the electrolyte

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(Equation 1), limiting the electrolyte to aqueous solutions. In aprotic electrolytes based on organic solvents or ionic liquids, only double-layer charging is observed leading to very poor charge storage.



In previous work, however, we demonstrated that the range of electrolytes required to support pseudocapacitance in RuO_2 and MnO_2 could be extended to ionic liquids provided they contain labile protons.[12–14] Protic ionic liquids are obtained from the proton transfer of a Bronsted acid to a base and, provided that the pKa difference between both proton donor and acceptor is sufficiently large, they show low volatility and high boiling point similar to their aprotic counterparts.[15–17] These protic ionic liquids have been successfully applied to EDLC electrolytes,[18–21] but little is known about their interactions with metal oxides for pseudocapacitors. In our previous studies, 12 protic ionic liquids were obtained using the trifluoroacetate anion with different heterocyclic bases, and despite the very different conductivities, viscosities, and thermal and electrochemical stabilities, all PIL provided the same specific capacitance in RuO_2 within the limits of experimental error, although these values were very close to the reference of 40–45 F/g obtained in 0.5 M H_2SO_4 . [12,13] Such low specific capacitance values were obtained with a highly crystalline RuO_2 electrode obtained by thermal decomposition (400 °C) of a solution of a RuCl_3 precursor salt. Such crystalline structure provides a high electronic conductivity but much lower specific capacitance compared to the hydrated material obtained by hydrothermal methods.[22] This observation suggested that the limitations to the amount of energy being stored in RuO_2 -PIL systems could be related to the structure of the electrode and a difficult access of the electrolyte to the material active sites. The research that is presented here was carried out to determine the impact of a composite electrode of hydrated RuO_2 material, of electrolyte viscosity and composition, and of temperature on the specific capacitance in a protic ionic liquid. The protic ionic liquid diethylmethylammonium-triflate, abbreviated as DEMA-TfO, was selected for its high stability and ionicity which are resulting from the large pKa (values from aqueous solutions) difference between the diethylmethylamine (~10) and trifluoromethanesulfonic acid (-12 to -15). Such large ΔpKa are required to disfavor the backwards charge neutralisation reaction and favor high ionicity and high boiling point in protic ionic liquids.[15] DEMA-TfO was studied before as a non-aqueous proton transfer media and an example of its application in fuel cells working under non-humidifying conditions was provided.[23] It is thermally stable up to 360 °C and possesses a good ionic conductivity, around 10 mS cm^{-1} at room temperature, making it a promising electrolyte for metal oxide pseudocapacitors. The ionic liquid was used in its pure, undiluted form as well as in mixtures with acetonitrile to reduce electrolyte viscosity. The RuO_2 active material was incorporated in composite electrodes rather than in thin films, as in our previous work, to increase the material loading and to study the effect of the composition on the specific capacitance. Finally, the electrochemical response of RuO_2 composite electrodes was studied at temperatures up to 120 °C, taking advantage of the thermal stability and low volatility of DEMA-TfO.

2. Experimental

2.1. Chemicals

All materials were obtained from Sigma-Aldrich except for trifluoromethanesulfonic acid which was purchased from Synquest Laboratories. They were all obtained with the higher purity available and used without further purification.

2.2. RuO_2 electrodes

Ruthenium oxide powder was prepared by the sol-gel method proposed by Zheng and Jow,[22] which consists in precipitating $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$ from a RuCl_3 solution by increasing the pH with NaOH. The powder was then annealing at 150 °C for 17 hours in an oven to reduce the amount of water to $\text{RuO}_2 \cdot x\text{H}_2\text{O}$, where x is ca. 0.5, based on the temperature selected.[22] This material will be referred to as RuO_2 from hereon. Afterwards, composite electrodes were obtained by mixing the RuO_2 powder with the PTFE at 10 wt.% in a mortar, to form a paste that was pressed on a stainless steel gauze used as current collector.

2.3. Diethylmethylammonium-triflate protic ionic liquid

The DEMA-TfO protic ionic liquid was prepared by the slow addition of trifluoromethanesulfonic acid into diethylmethylamine to reach an equivalent molar ratio of base and acid, under continuous stirring. An ice bath was used to keep the mixture cool (exothermic proton transfer reaction). Water was removed by heating the protic ionic liquid under vacuum at 80 °C for 12h. The amount of water contained in the PILs was determined using a coulometric Karl-Fisher titrator from Mettler Toledo (model C30) and HYDRANAL®-Coulomat AG as the reagent. The values obtained for two different drying conditions were 0.17 and 0.88 wt.%. A third sample was prepared by adding water to a dried DEMA-TfO to reach 5 wt.%. Unless stated otherwise, the results are presented for the sample containing 0.88 wt.% of water.

2.4. Electrochemistry

The electrochemical window of stability of the DEMA-TfO was determined on a Pt electrode (BAS, 0.0249 cm^2) using a PAR-STAT 2273 or a Biologic VMP3, which were also used for all other electrochemical measurements. The capacitive behavior of the RuO_2 electrodes in the protic ionic liquids and their mixtures was investigated using a homemade heart-shaped electrochemical cell. An Ag/AgCl reference electrode (3 M KCl) was used for the measurements done in aqueous H_2SO_4 solutions and an Ag wire quasi-reference electrode (AgQRE) was used for measurements in ILs in order to avoid electrolyte contamination by water. A spiral of Pt wire was used as the auxiliary electrode in both cases. The RuO_2 electrodes were equilibrated prior to all measurements by doing 20 cycles in the electrolyte. The electrolytes were degassed for at least 15 min with nitrogen before the experiments. All measurements were carried out at RT.

2.5. Surface analysis of RuO_2 electrodes

Spectra were recorded with a VG Escalab 3 MKII apparatus equipped with an Mg K_α monochromatic source ($h\nu = 1253.7$ eV, 12.5 kV) and a hemispherical analyzer with a multi-channel detector. The pressure in the main chamber was maintained to approximately 1×10^{-9} Torr during the analysis. Survey and high-resolution spectra were obtained with pass energies of 100 and 20 eV and resolutions of 1.0 and 0.05 eV, respectively.

3. Results and Discussion

3.1. Behavior of ruthenium dioxide in DEMA-TfO

The electrochemical window of stability of the pure DEMA-TfO was firstly evaluated by cyclic voltammetry using a Pt working electrode. The CV scan obtained, presented in Fig. 1, shows a window between -0.3 V and +2.3 V, against an Ag wire quasi-reference electrode (AgQRE) which is ca. +0.08 V vs. Ag/AgCl (calibrated

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