Capacitance characteristics of carbon-based electrochemical capacitors exposed to heteropolytungstic acid electrolyte

Magdalena Skunik-Nuckowska [a, *], Sławomir Dyjak [b], Katarzyna Grzejszczyk [a], Natalia H. Wisińska [a], François Béguin [c], Pawel J. Kulesza [a, **]

[a] Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland
[b] Institute of Chemistry, Military University of Technology, Urbanowicza 2, 00-908 Warsaw, Poland
[c] Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Berdychowo 4, Poznan, Poland

ABSTRACT

A Keggin-type heteropolytungstic acid, $H_3PW_{12}O_{40}$, is evaluated as new high ionic conductivity aqueous electrolyte of potential interest for electrochemical capacitors, with enhanced safety and low environmental concern. For the performance evaluation, two types of electrode materials have been selected, i.e. mesoporous multi-walled carbon nanotubes and microporous activated carbons. To address the influence of changes in the porous structure and surface properties on capacitors performance, the materials have been subjected to additional oxidation treatment under liquid or gas phase conditions. The electrochemical parameters of two-electrode cells were evaluated from a series of voltammetric, galvanostatic, constant power, and AC impedance measurements and compared with those obtained for conventional H_2SO_4 electrolyte. It has been shown that due to the size of the heteropolytungstate anion (exceeding 1 nm), the selection of carbon electrode materials in terms of appropriate porous structure and wettability is a key factor in avoiding capacitance limitations. As a result, the specific capacitance, energy density as well as the rate capability of $H_3PW_{12}O_{40}$ supported capacitors may approach the performance of conventional H_2SO_4-based systems. Furthermore, the potentiodynamic anodic polarization tests and post-mortem scanning electron microscopy analysis confirmed a higher corrosion resistance of 316 L type steel in the presence of $H_3PW_{12}O_{40}$ solution, in comparison to the conventional H_2SO_4 electrolyte. It enables stable capacitor performance upon utilization of low cost non-noble current collectors which was evaluated during galvanostatic cycling (13 000 cycles) and accelerated ageing by potentiostatic floating during 120 h.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

The increasing cost and depletion of fossil fuels, together with rising emission of carbon dioxide and growing demand for fast and efficient energy storage systems, induced by the development of portable electronics or electric automobiles, stimulate interest in high-performance electrochemical capacitors (ECs). The principle of operation of the simplest electrical double-layer capacitor (EDLC) involves electrostatic adsorption of the electrolyte ions within the micropores of high surface area carbon materials, which results in

10–100 times higher power density than for batteries, energy efficiency close to 100% and stability up to million cycles of continuous operation [1,2]. Typically, the commercially available cells use organic electrolytes such as acetonitrile or propylene carbonate with the addition of ionically conductive salts, providing a wide voltage window of 2.7–2.8 V, resulting in high energy density. However, such disadvantages as low ionic conductivity, toxicity, sensitivity to moisture and oxygen and fairly high cost cannot be neglected [3,4]. Therefore, there is a growing research interest on aqueous electrolytes, offering several benefits such as higher ionic conductance, lower viscosity, enhanced safety and possibility of cost-effective production. Among a large number of aqueous electrolytes, sulfuric acid is still one of the most commonly used, despite it could also be hazardous, and its use requires expensive current collectors of increased corrosion resistance. Hence, other types of aqueous electrolytes have been recently intensively

---

investigated including alkali metal salts which with respect to the operating voltage and energy density enable to approach the performance of organic systems [5–12]. However, their ionic conductivity is noticeably lower than for typical acidic or alkaline electrolytes such as H_2SO_4 and KOH, leading to a rise of the overall series resistance [13].

The present study is focused on investigating alternative aqueous electrolyte for ECs utilizing Keggin-type tungsten polyoxometalates (POMs). POMs are a large group of inorganic compounds formed by transition metal oxides clusters (typically of Mo, W or V) in the highest oxidation states, existing in a variety of architectures, sizes and compositions. Their interesting chemical and well-defined molecular properties have been successfully used in catalysis, electrocatalysis, photovoltaics, medicine as well as for the construction of sensors and photochromic devices [14–24]. Also, the charge storage properties of POMs-containing electrodes and devices have been widely demonstrated [25–31].

The heteropolytungstic acid ($H_3PW_{12}O_{40}$), selected here as a model representative of Keggin-type POMs, is a strong, fully dissociated Brönsted superacid, characterized by high ionic conductivity (on a level of $0.25\,S\,cm^{-1}$ for ca. $0.5\,mol\,dm^{-3}$ aqueous solutions [32,33]) and known as one of the most chemically and thermally stable POM compounds. It is easily obtainable from the acidified solutions of alkali metal tungstates and phosphoric acid and well soluble in polar solvents. Furthermore, it is relatively non-toxic, which might be of importance with respect to safety, simplicity of handling and disposal [14,34]. And finally, as further demonstrated, in contrast to sulfuric acid, it is much less aggressive toward stainless-steel, which should make less-expensive current collectors applicable.

The concept of applying Keggin-type POMs as electrolytes for charge storage applications has been for the first time reported by K. Lian et al. [35–39]. Cells utilizing aqueous or poly (vinylalcohol)-based polymer electrolytes doped with tungsten or silicon-type POMs, sandwiched between bare or graphite conductive ink coated stainless-steel current collectors, exhibited an exceptionally high rate capabilities and very good electrochemical and thermal stability. However, since low specific surface area graphite ink was the only carbon material tested, the specific capacitance (expressed per electrode area) was on the level of only $1\,mF\,cm^{-2}$. Moreover, the POM-type electrolyte performance at the interface with practical capacitive-type electrodes, i.e. highly porous carbons is so far barely known. Meanwhile, due to the fairly large size of the $PW_{12}O_{40}^{3-}$ ion, the choice of the electrode material and its porosity seem to be of primary importance. The X-ray diffraction analysis of $H_3PW_{12}O_{40}$ crystals clearly shows that the structure of the anion is polyhedral (typically tetragonal), rather that spherical (or octahedral), which leads to some variation in the diameter with the direction of measurement, namely from 1.027 to 1.197 nm [40]. The effective size of the polyanion in solution is obviously difficult to estimate, however, existing data indicate that its hydrodynamic radius in aqueous medium is on the level of 0.56–0.58 nm. What is also important, due to its size, and consequently low hydration energy, the polyanion remains unsolvated, or barely solvated, in aqueous solution [33,41]. Thus to comment about capacitive properties in $PW_{12}O_{40}^{3-}$-containing solutions, electrochemical investigations should be performed with highly developed surface area electrode materials. Under such conditions, one should be able to evaluate to which extent the microporous material is able to host the electrolyte anion during the electrical double-layer charging/discharging processes.

In the present work, we pursue a study of the electrochemical properties of ECs utilizing activated carbons as electrode materials together with heteropolytungstic acid as electrolyte. The materials have been intentionally subjected to chemical and thermal modifications, involving HNO_3 and air treatments, in order to tailor their interfacial properties toward adequate porosity and enhanced wettability. The charge transport dynamics in $H_3PW_{12}O_{40}$ electrolyte has been diagnosed using AC impedance spectroscopy and constant power discharging. A direct comparison to the results obtained in conventional H_2SO_4 electrolyte is provided. The diagnostics and investigations with mesoporous electrode materials, such as carbon nanotubes, where the size of $PW_{12}O_{40}^{3-}$ should not be a limiting factor, is also considered. Furthermore, the choice of current collectors in terms of their resistance to corrosion in presence of heteropolytungstic acid electrolyte is discussed on the basis of potentiodynamic anodic polarization measurements and microscopic analysis.

2. Experimental

2.1. Materials preparation

Multi-walled carbon nanotubes (outer diameter: 10–15 nm, inner diameter: 2–10 nm, length: 0.1–10 μm), polytetrafluoroethylene (PTFE, 60 wt% dispersion in H_2O) and heteropolytungstic acid ($H_3PW_{12}O_{40} \cdot 6\,H_2O$, 12.4 wt% of physisorbed water, Fig. S1) were obtained from Sigma-Aldrich. The activated carbon Norit SX2 was purchased from POCH (Polish Chemical Reagents). The conductive carbon black Super C65 and porous glassy fibrous separator (GF/A, thickness 260 μm) were supplied by Imerys Graphite&Carbon and Whatman®, respectively. The activated carbon Norit SX2 (further referred to as AC-1) was oxidized for 5 h under reflux in $3\,mol\,dm^{-3}$ HNO_3 (AC-2), and in air at 425 °C (AC-3). The heating rate was $5\,°C\,min^{-1}$. Carbon nanotubes (CNT-1) were subjected to HNO_3 treatment under mild conditions, for only 2 h (CNT-2), in order to avoid structural defects in nanotubular structure. .

Pellet electrodes consisted of 90 wt% pre-dried carbon material (AC or CNTs), 5 wt% carbon black and 5 wt% PTFE. The samples of known weight (ca. 11 mg for CNTs and 13–16 mg for AC) were pressed under 5 tons per cm^2 for 60 s and dried under vacuum at 120°C overnight. The electrodes (geometric area: 0.785 cm^2, thickness: 300 ± 20 μm (AC) and 350 ± 20 μm (CNT)) separated by a glassy fibrous separator were assembled between 316 L stainless steel or gold current collectors in a Swagelok®-type cell equipped with a reference Ag/AgCl electrode and filled with the electrolyte which was aqueous solutions of either $H_3PW_{12}O_{40}$ (0.1–0.8 $mol\,dm^{-3}$) or $1\,mol\,dm^{-3}$ H_2SO_4.

2.2. Physicochemical characterizations

The N_2-physisorption measurements were performed at liquid nitrogen temperature using a Micromeritics ASAP 2020 apparatus. Prior to the measurements, the samples were outgassed for 12 h at 473 K under high vacuum. The Brunauer, Emmett and Teller specific surface area (SSA) was calculated from the N_2 adsorption isotherm where the p/p_0 range was selected individually for each isotherm to obtain the best linear fit of the BET plot, according to IUPAC recommendations [42]. The total pore volume (V_t) was estimated from the volume adsorbed at a relative pressure of 0.99. The volume of micropores (V_{mi}) and the pore size distributions (PSDs) were calculated using the density functional theory embedded in the SAIEUS software: 2D-NLDFT model for heterogeneous carbon surfaces of ACs and 2D-NLDFT cylindrical model for carbon nanotubes were applied. The volume of mesopores (V_{mes}) was determined as the difference: $V_{mes} = V_{total} - V_{mic}$. The specific surface area of micropores (S_{mic}) was calculated using the t-plot method with the reference to standard nitrogen adsorption data for non-porous carbon [43] and S_{ext} as the difference $S_{BET} - S_{mic}$. The average