



Performance of metal oxide nanoparticle sols as binders in activated carbon electrodes



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ABSTRACT

The primary purpose of this study was to evaluate the performance of composites, as electrode materials, made with activated carbon (AC) and SiO₂ or γ -AlOOH gels as binders and compare these to traditional electrodes fabricated with AC and polyvinylidene fluoride (PVDF). Electrodes made out of AC and SiO₂ or γ -AlOOH composites showed a much better wear resistance than those fabricated with AC and PVDF composites. Furthermore, cyclic voltammetry and chronopotentiometric measurements showed that the electrodes using oxides as binders had an electrochemical capacitance between 2 and 5 times higher than those made with AC and PVDF composites. This higher electrochemical capacitance is based on the fact that composites that use SiO₂ and γ -AlOOH as binders exhibit a much higher specific surface area and water hydrophilicity than those containing PVDF. The addition of PVDF to the AC decreases its specific surface area by a factor of seven. In contrast, the addition of SiO₂ or γ -AlOOH gels to the AC powder slightly increases the surface area. Scanning electron microscopy (SEM) images showed that the AC particles are coated with a nanoporous layer of these metal oxides.

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1. Introduction

As global population continues to rise, the need for clean and renewable energy will follow. Consequently, the demand for energy storage devices associated with renewable energy sources, such as wind and solar power will also increase [1]. Electrochemical capacitors (also called supercapacitors or ultracapacitors because of their extremely high capacitance) have attracted significant attention due to their high power densities, long cycle life, safety, environmental friendliness and wide range of operational temperatures [1]. The large capacitances associated with these devices can be attributed to the high surface area materials used as electrodes, since charge is stored in the electric double layer at the interface between these high surface area electrodes and a liquid electrolyte [2]. Supercapacitors are used in many commercial applications including backup systems, hybrid

energy for electrical vehicles and in space [1,3]. Additionally, they are also employed in capacitive deionization (CDI), an emerging water treatment technology that uses an applied potential or current between a pair of electrodes, to remove ions from water and at the same time store energy. Moreover, the ability of CDI to deionize water and store charge may allow it to overcome some of the drawbacks of traditional desalination technologies such as reverse osmosis, electro dialysis and ion exchange [4,5].

One major factor that determines the performance of these supercapacitors is the properties of the materials used for the electrode. A variety of carbon materials have been investigated for supercapacitor applications, these would include carbon aerogels [6], xerogels [7], cryogels [8] and nanofoams [9,10]. However, the most widely used material is high surface area activated carbon (AC) because of its abundance, low cost, chemical stability, ease of processing, favorable electrical conductivity and wide temperature range of operation [11]. Furthermore, controlled surface areas and pore distributions, which alter the electrode/electrolyte interface for electrochemical applications, can be obtained with various established chemical and physical methods [3]. In order to manufacture electrodes from AC powder, a binder is needed to provide the adhesion at the particle/particle interface. Moreover,

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binders also have to bind the composite electrode film to the current collector. In general, binders that have been utilized in carbon electrode fabrication are typically organic polymers (e.g. polyvinylidene chloride (PVDC) [12], Teflon [13], polytetrafluoroethylene (PTFE) [10,14]), with the binder content varying from 5 to 20 wt%. Higher binder content increases adhesion strength between the carbon particles, but also decreases electronic conductivity. Several authors have argued that increasing the binder content lowers the capacitance and electro-sorption capabilities of the electrode; they attributed this decrease in performance to the clogging of carbon nanopores with a subsequent decrease in specific surface area of the electrode [12,15,16]. It has also been reported that the use of organic binders could affect the series resistance and limit the power capability of the electrochemical capacitor [17]. The negative effects caused by polymeric binders have prompted research on how to fabricate carbon supercapacitors without the use of binders, with several alternatives being suggested [16]. Do et al. claimed that binder-free carbon electrodes could be fabricated using single walled carbon nanotube-activated carbon composites [18]. Another report suggested the use of several micrometer thick layers of nano-structured carbon onions to prepare a carbon electrode without the addition of an organic binder [19]. Yet another example of a binder free supercapacitor was investigated by Xu et al. where a composite ink of graphene/polyaniline was used to print supercapacitors [20,21].

The aim of this study is to develop AC powder electrodes without organic binders. To accomplish this task, the AC particle/particle cohesion strength will be provided by a gel (continuous network of nanoparticles) of either SiO_2 or Al_2O_3 . These composites are prepared by mixing AC particles with an aqueous sol of either SiO_2 or $\gamma\text{-AlOOH}$ nanoparticles. Upon drying the composite, the AC particles should be imbibed in a gel of oxide particles. Sintering the composites in the temperature range between 300 and 400 °C could further increase the adhesion strength between AC particles. Moreover, the specific surface area of these composites is expected to be much larger than the polymeric composites as these xerogels exhibit high specific surface area [22], one or two orders of magnitude higher than polymeric binders such as polyvinylidene fluoride (PVDF) [23]. In addition, it has been reported that these nanoporous metal oxides are capable of increasing the capacitance of a variety of carbon materials [10,22,24]. Leonard et al. found that metal oxide nanoparticle coatings, such as SiO_2 or $\gamma\text{-AlOOH}$, attract ions existing in the electrolyte onto the surface of the electrode because of their intrinsic surface potential [10,24]. In this fashion, one is able to increase the concentration of counter ions at the electrolyte surface interface. One of the few experimental ways to estimate the surface potential is to measure the zeta potential, but zeta potential is only a surrogate indicator of surface potential as this value depends on ionic strength. For constant potential surfaces, which all oxides represent, potentials are fixed by pH (proton concentration) and the specific adsorption of other potentially determining ions. On the other hand, surface charge increases with an increase in ionic strength. In addition, metal oxides, especially non-transition metal oxides, are inexpensive materials and are easily prepared through sol-gel processes [24]. However, these earlier studies, while revealing the advantages of coating a metal oxide onto carbon based electrodes, did not utilize the metal oxide nanoparticles as a binder in the electrode fabrication process.

In this study, different slurry pastes were coated onto a current collector. The different pastes consisted of activated carbon powder and graphite mixed with either PVDF, SiO_2 sol or $\gamma\text{-AlOOH}$ sol. The graphite was used to improve the conductivity of the composite carbon electrodes. Physical characteristics (morphology, pore structure, thermal properties and physical strength) and

electrochemical properties (potentiostatic measurements and galvanostatic measurements) were examined for AC powder-based electrodes containing either SiO_2 nanoparticles, $\gamma\text{-AlOOH}$ nanoparticles or a traditional organic binder. In addition, selected electrodes, consisting of either of the aforementioned metal oxide composites, were dipped into SiO_2 or $\gamma\text{-AlOOH}$ sols, and the resulting physical and electrochemical properties were also measured and compared to those not coated.

2. Experimental

2.1. Electrode fabrication

The AC electrodes consist of five layers: a current collector, a thin layer of graphite and organic binder (referred to as the bonding or adhesion layer) on each side of the collector (2 layers total, one on each side of the current collector), and a thick layer of the different AC composites studied in this paper on top of each bonding layer (2 layers total, one on top of each of the bonding layers). In addition, a few of the electrodes were prepared without the adhesion layers.

2.1.1. Current collectors

A graphite foil (Alfa Aesar) cut to 4 cm² (0.254 mm thick) was used as the current collector. The graphite collectors were heated at 300 °C for 1 h to increase wettability.

2.1.2. Bonding layers

Current collectors were coated with a mixture of organic binder and graphite powder using a dip-coating technique. The collector foil was dipped into a suspension of the mixed organics and withdrawn at a velocity of 2.5 mm s⁻¹. The organic suspension consisted of a *N*-methyl-2-pyrrolidinone solution (NMP) (Sigma-Aldrich), PVDF (molecular weight = 180,000, Aldrich Chemical Co.) and graphite powder (1–2 μm, synthetic, Aldrich Chemical Co.) with a ratio of 12.85:1:1.5 wt%. The coated samples were then dried in an oven at 80 °C for 1 h or until the NMP solution was completely removed.

2.1.3. Nanoparticle suspensions

The SiO_2 nanoparticle sols were prepared following the method described in Chu et al. [25]. The final pH of the SiO_2 sol was 3, concentration of approximately 30 g l⁻¹, and the size of the SiO_2 particles in suspension below 5 nm. The $\gamma\text{-AlOOH}$ nanoparticle sols were prepared using methods from Schultz et al. [26] and modified by Wouters et al. [22]. The final concentration was approximately 20 g l⁻¹ and the size of the $\gamma\text{-AlOOH}$ particles in suspension were between 5 and 8 nm.

2.1.4. AC composite layer

The elemental carbon mixture of all composites consists of granular AC (Sigma-Aldrich, 12–20 mesh) and graphite powder with a ratio of 90:10 wt%. Two of the AC composites, named “AC- SiO_2 ” and “AC- $\gamma\text{-AlOOH}$ ”, were prepared by mixing SiO_2 sol or $\gamma\text{-AlOOH}$ sol with the above mentioned elemental carbon mixture with a ratio of 10:90 wt% (10% referring to the weight of the dried xerogel). Two other AC composites were made with a traditional organic binder, PVDF, instead of the metal oxide nanoparticles, by following the same procedure described above. NMP solution with dissolved PVDF was used as a substitute for the metal oxide nanoparticles sol in this fabrication process (with 10% and 20% of PVDF: named “AC_10% PVDF” and “AC_20% PVDF”). All four composites were placed into a ball mill and milled for 1 day. A predetermined quantity of the resulting slurry was coated on top of each bonding layer or directly onto the collector foil without bonding layers. The quantity of deposited

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