Carbon 123 (2017) 318–333

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

High-performance activated carbon from polyaniline for capacitive deionization

Rafael L. Zornitta [a, *], Francisco J. García-Mateos [b], Julio J. Lado [a, c], José Rodríguez-Mirasol [b], Tomás Cordero [b], Peter Hammer [d], Luis A.M. Ruotolo [a, **]

[a] Department of Chemical Engineering, Federal University of São Carlos, Rod. Washington Luiz km 235, 13565-905, São Carlos, SP, Brazil
[b] Department of Chemical Engineering, Andalucía Tech, University of Málaga, Campus de Teatinos s/n, 29010, Málaga, Spain
[c] Madrid Institute for Advanced Studies, IMDEA Energy, (Electrochemical Processes Unit), 28933, Móstoles, Madrid, Spain
[d] Institute of Chemistry, São Paulo State University – UNESP, Rua Prof. Francisco Degni, s/n, 14800-900 Araraquara, SP, Brazil

ARTICLE INFO

Article history:
Received 28 March 2017
Received in revised form
10 July 2017
Accepted 21 July 2017
Available online 24 July 2017

ABSTRACT

Activated carbons prepared using polyaniline (PAni), a N-containing precursor, doped with different anions were successfully employed in this work as electrode materials for capacitive deionization. The aim of this research was to investigate the effect of chloride (Cl^-), *p*-toluenesulfonate (PTS^-), dodecylbenze-sulfonate (DBS^-) and polystirenesulfonate (PSS^-) as PAni dopants on the textural and electrochemical properties of PAni activate carbon (PAC) and evaluate their performance for desalination. It was demonstrated that textural PAC properties such as microporosity could be properly tuned, resulting in a suitable proportion of micro- and mesoporosity by using different doping anions. Furthermore, it was observed that the higher the oxygen content the higher the electrode hidrophilicity due to introduction of surface polar groups, as identified by XPS. These groups were found to be the most important variable influencing on the PAC electrosorption capacity and energy efficiency. The highest specific adsorption capacity (14.9 mg g^{-1}), along with the lowest specific energy consumption, was obtained using the PTS-doped PAC electrode. Considering its high capacity, low-cost and ease of synthesis, PAC/PTS seems to be a promising electrode for CDI.

1. Introduction

Water scarcity as result of population growth and industrialization has become one of the major issues of the 21st century. Despite the large reserves of water still available on earth (e.g. seawater and groundwater), great part of this water does not meet quality standards for human consumption mainly due to the high concentration of salts. To make water drinkable, reverse osmosis (RO), electrodialysis (ED), and multi-effect distillation (MFD) can be employed for water desalination, although these technologies demand high energy consumption in large-scale applications [1,2]. In this context, CDI has emerged in the last few years as a low-cost technology that can be used to remove ions from brackish water (~10,000 mg L^{-1}), but consuming less energy than its main competitor, the RO [2]. CDI is based on the concept of charge storage in the electric double layer (EDL) developed when ions are attracted to a pair of porous carbon electrodes when an external voltage is applied. The low energy consumption of CDI comes from the low voltage needed for the electrosorption process (typically 1.0–1.4 V) and the low required pressure when compared to RO [3–5]. After electrode saturation, the regeneration of the electrodes is achieved by short-circuiting the cell [4,6]. Another possibility is to invert the cell potential repelling the electrosorbed ions, thus reducing the time needed for electrode regeneration (Fig. S1) [5].

Despite the advantages presented by CDI relative to other well-established technologies like RO and ED, there are still challenging issues, such as electrode material, to be overcome in order to make this technology feasible for large-scale applications. The electrode material for CDI must have fast electrosorption kinetics and high adsorption capacity. A good candidate for electrode material to be used for CDI must have high specific surface area (SSA) available for electrosorption, high conductivity, good wettability, fast response to polarization, and chemical stability [7]. Carbon materials fit most

* Corresponding author.
** Corresponding author.
E-mail addresses: rafael_rlzs@hotmail.com (R.L. Zornitta), pluis@ufscar.br (L.A.M. Ruotolo).

http://dx.doi.org/10.1016/j.carbon.2017.07.071
0008-6223/

of these requirements and have been intensively used as CDI electrodes, e.g., carbon aerogels [3,8,9], mesoporous activated carbon [4,10], microporous activated carbon [11], carbon felts [12], carbon fibers [13], carbon nanotubes [14,15] and their modification using oxides [16,17] and conducting polymers [18,19]. Although there are many studies related to electrode materials for symmetrical membraneless CDI, the carbons showing the best performance, such as nitrogen doped graphene, are still too expensive and in many cases their preparations are not environmental friendly [20].

Recently, nitrogen-doped activated carbons (N-doped AC) have been reported to enhance CDI electrode performance [21–24] mainly due to the (i) introduction of defects and distortion in the carbon matrix, facilitating the ion access to the surface area and increasing charge accumulation, (ii) enhancement of charge density due to the presence of nitrogen, which facilitates the charge-transfer process [24,25], and (iii) introduction of surface groups responsible for pseudocapacitance [21]. CDI materials reported to exhibit the highest specific adsorption capacity (SAC) are N-doped graphene (21.9 mg g^{-1}) [21], N-doped graphene sponge (21 mg g^{-1}) [25], and N-doped cotton-derived carbon sponge (16.1 mg g^{-1}) [24]. The most common approach to introduce N-groups into the carbon structure is the post-treatment with ammonia at high temperatures. However, this technique leads to a low nitrogen content and poor thermal stability [26]. Moreover, this process could become too expensive considering the precursor preparation followed by the activation with ammonia.

Nitrogen-containing precursors such as glucosamine hydrochloride [23], polyacrylonitrile [27], PAni [28–30] and polypyrrole [31] have become a low-cost alternative to obtain N-doped AC dispensing the post-treatment. Among these materials, PAni find applications in different fields such as supercapacitors [32], cation exchange [33], and as additive to improve AC capacitance in CDI [19,34]. PAni presents high nitrogen-content (~15 wt%), it is inexpensive, easily synthetized, and has a structure similar to graphite, which could facilitate the introduction of nitrogen-containing active sites inside the carbon matrix at high temperatures [30,35]. Furthermore, the PAni properties can be easily customized by varying the doping anion during the polymerization process [36]. The use of PAni as AC precursor has already been reported for different applications such as adsorption [37], supercapacitors [29,30,36,38–45], electrocatalysts [35,41], and batteries [45]; however, to the best of our knowledge, PAC has never been used for CDI applications.

PAC has been considered a promising material for electrochemical applications due to its distinguished structural and textural characteristics. Recent studies have shown that depending on the precursor synthesis and activation method, PAC presents extremely high SSA [37,44,45], high mesopore volume [40], high capacitance [29,43], good wettability [43], and long-term stability [29,30]. The presence of quaternary nitrogen in the carbon matrix can enhance the charge-transfer, thus improving the CDI electrode conductivity [24,25]. Moreover, the presence of pyridine- and pyrrole-like nitrogen groups is recognized as being responsible to create pseudocapacitance [21] and also to improve carbon wettability due to the redox reaction with water according to Equation (1) [25,46].

$$-CH = NH + 2e^- + H_2O \rightleftharpoons -CH - NHOH$$

In this scenario, the application of PAC as CDI electrodes seems to be promising and was the aim of this investigation. To the best of our knowledge, the use of PAC for CDI using PAni doped with different anions is reported for the first time. PAni was used as N-containing precursor to obtain a N-doped AC. Furthermore, the effect of the large (dodecylbenzene-sulfonate, DBS^-, and polystirenesulfonate, PSS^-) and small dopant anions (Cl^- and *p*-toluenesulfonate, PTS^-) on the textural properties of the obtained PAC was compared.

In order to understand the effect of different anions on the PAC electrode performance for desalination, PACs were characterized regarding to their SSA, pore size distribution (PSD), morphology, surface functional groups, electrochemical capacitance and charge-transfer resistance. The desalination performance was evaluated in terms of electrosorption kinetics, SAC, charge efficiency and specific energy consumption. The results confirmed the great potential of this novel approach to explore the properties of PAni to obtain tailorable N-doped activated carbons for CDI electrodes.

2. Experimental

2.1. Materials

The monomer aniline (99% Sigma-Aldrich) was distillated prior to use for polymerization and maintained in amber bottle at low temperatures (<3 °C) to prevent oxidation. Anion sources used as counter ions for polyaniline were hydrochloric acid (HCl, 36.5–38%, J.T. Baker), *p*-toluenesulfonic acid monohydrate (HPTS, ≥98.5%, Sigma-Aldrich), sodium dodecylbenzene-sulfonate (NaDBS, Sigma-Aldrich) and poly(4-styrenesulfonic acid) (HPSS, 18 wt % solution in water, Sigma-Aldrich). The oxidant used for polymerization was ammonium persulfate (98%, Sigma-Aldrich). Polyvinylidene fluoride (PVDF, Sigma Aldrich) and n-methylpyrrolidone (NMP, 99.5%, Synth) were used as binder and solvent, respectively, for electrode preparation. Commercial activated carbon (CAC) YP-50F was purchased from Kuraray Corp., Japan.

2.2. Polyaniline synthesis

PAni was chemically synthesized using the optimized conditions adapted from Jelmi et al. [47] Briefly, 10 mL of aniline (0.21 mol L^{-1}) was added at low temperature (~3 °C) and constant stirring to 500 mL solution containing 0.30 mol L^{-1} of the doping compounds (HCl, HPTS, NaDBS and HPSS). The polymerization started adding 85.9 mL of the oxidant solution ($(NH_4)_2S_2O_8$ 1.0 mol L^{-1}), dropped slowly into the monomer solution. The mixture was left to react for 24 h under stirring. After polymerization, the precipitated PAni doped with Cl^- and PTS^- were filtered, washed with acid solution (HCl and HPTS, respectively) and dried in oven at 60 °C for 24 h [43]. Regarding to PAni doped with DBS^-, 750 mL of acetone (99.5%, Synth) was added to the polymerization solution to precipitate the polymer particles, followed by filtration and washing with plenty of water and dried in oven at 60 °C for 24 h [48,49]. The particles of PAni doped with PSS^- were separated by leaving the polymerization solution in an oven for 24 h at 60 °C to evaporate the solvent [50]. The samples of PAni doped with the different anions were referred as PAni/Cl, PAni/PTS, PAni/DBS and PAni/PSS.

2.3. Polyaniline carbonization and activation

PAni was activated according to the procedure adapted from Yan et al. [29]. In this procedure, PAni was firstly carbonized in a tubular furnace (Thermo Scientific Lindberg Blue M) at 850 °C at a heating rate of 10 °C min^{-1} for 2 h under N_2 atmosphere (150 mL min^{-1}). After carbonization, the samples were activated with KOH in a proportion of 1:4 (polymer:KOH, w/w) followed by heating at 850 °C for 1.5 h using the same heating rate and N_2 flow conditions of the carbonization process. The ratio 1:4 (w/w) of carbonized carbon to KOH was chosen based on previous studies reporting an