New Nanostructures as novel electrodes in Capacitive deionization desalination Technology

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ABSTRACT

Among the various carbonaceous materials which are widely exploited as electrodes, graphene revealed good performance due to its marvelous electrical properties and high surface area. In this study, metallic nanoparticles encapsulated in a graphite shell (Cd-doped Co/C NPs) are introduced as novel electrodes for the capacitive deionization process. Compared to graphene, Cd-doped Co/C NPs showed better performance. Moreover, the charge-discharge analysis indicated good stability and recyclability of the introduced NPs. The introduced NPs have been synthesized using a simple sol-gel technique. The utilized physiochemical characterizations affirmed that drying, grinding and calcination in Ar atmosphere of the prepared gel leads to produce Cd-doped Co nanoparticles encapsulated in a thin graphite layer.

Keywords: Capacitive deionization, Water desalination, Bimetallic nanoparticles, Capacitance, Nanoparticles.

1   INTRODUCTION

Capacitive deionization (CDI) is an emerging water treatment technology that uses electrophoretic driving forces to achieve desalination. During CDI, ions are adsorbed onto the surface of porous electrodes by applying a low voltage (1.0-1.6 VDC) electric field. The negative electrodes attract positively charged ions such as calcium, magnesium, and sodium simultaneously; the positive electrodes attract negatively charged ions such as chloride, nitrate and sulfate [1-5]. Unlike ion exchange processes, no additional chemicals are required for regeneration of the electrosorbent in this system. Eliminating the electric field allows ions to desorb from the surface of the electrodes and regenerates the electrodes. There are a variety of electrode materials and configurations to enhance performance. Previous studies show that CDI technology is cost competitive with reverse osmosis processes only at a low feed TDS concentration range (<3,000 mg/L) due to the high cost of CDI modules with increased feed water TDS concentration s. During laboratory and field treatment of sandstone-produced water with a commercial CDI system (Electronic Water Purifier (EWP)), no electrode deterioration was observed and the CDI process exhibited much less fouling/scaling propensity compared to RO/NF [6-8. Capacitive deionization (CDI) attracted enormous attention as an energy-saving and environmentally friendly desalination technique, it can be conducted at ambient conditions and low voltage without secondary waste, and does not require high-pressure pumps, membranes, desalination columns or thermal heaters [9]. A high capacitive electrode should have a high surface area for ionic accumulation, good electrical conductivity for effective charge holding, suitable pore size and good crosslinked structure for smooth ionic motions and electrolyte wetting [10, 11]. Carbon nanostructures reveal good performances as electrode materials for CDI. Recently, due to the distinct characteristics, some researchers have utilized graphene [7] and its composites [3, 12-15] as effective electrodes for the CDI, the results are better compared to other carbonaceous materials. In this study, we introduce metallic nanoparticles encapsulated in graphite shell to avoid the dissolution in water as novel electrode materials for the CDI technology. The introduced NPs revealed higher desalination performance compared to graphene.

2   EXPERIMENTAL

The introduced NPs have been synthesized using a sol-gel composedd of cobalt acetate (CoAc, 5%), cadmium acetate (CdAc, 1%), poly(vinyl alcohol) (PVA, 7%) and water (87%). The well mixed gel was dried in two successive steps. First, it was dried under atmospheric pressure at 60 oC for 24 h, and then under high vacuum atmosphere at 80 oC for 48 h. The obtained hard material was crushed and grinded. The calcination process was carried out under argon atmosphere at 1 atm and 700 $^{\circ}$C for 5 h with a heating rate of 2.3 $^{\circ}$C/min. The electrochemical measurements were performed on a VersaSTAT 4 (USA) electrochemical analyzer and a conventional three-electrode electrochemical cell. A Pt wire and an Ag/AgCl electrode were used as the auxiliary and reference electrodes, respectively. All potentials were quoted regarding to the Ag/AgCl electrode.

3 RESULTS AND DISCUSSION

The typical XRD pattern of the calcined powder is represented in Fig. 1, where the standard peaks of the cobalt are observed. The strong diffraction peaks at 2θ values of 44.35, 51.65, 75.95, 92.35 and 97.75° corresponding to (111), (200), (220) (311) and (222) crystal planes indicate the formation of cubic crystalline cobalt (JCDPS, card no 15-0806). Additionally, the broad peak at 2θ of 26.3° corresponds to an experimental d spacing of 3.37 Å indicates presence of graphite-like carbon (d (002), JCPDS; 41-1487). As can be concluded from the XRD spectra also, no cobalt oxides or carbides phases were present. Absence of any peaks related to cadmium compounds might be due to the small size of the produced cadmium-based nanoparticles (NPs). Thermo-gravimetric analysis (TGA) in argon atmosphere has been invoked to explain the mechanism of formation of pure cobalt from cobalt acetate/PVA composite. Actually, formation of pristine metal upon heating some metal acetate in an inert atmosphere was already reported [16]. The corresponding changes in the phase could be supported by thermo-gravimetric studies. Phase changes were construed by peaks in the first derivative of the TGA curve. Fig. 2 shows the TGA results for the utilized CdAc/CoAc/PVA powder in argon atmosphere. To precisely study these steps, the first derivative data were determined and demonstrated in the same figure. As shown in the first derivative data, there are many apparent peaks in the curve; the first and second (at ~70 and ~175 °C) can be assigned as liberating of physically (moisture) and chemically (combined water molecules with the CoAc and CdAc) water from the sample, respectively.
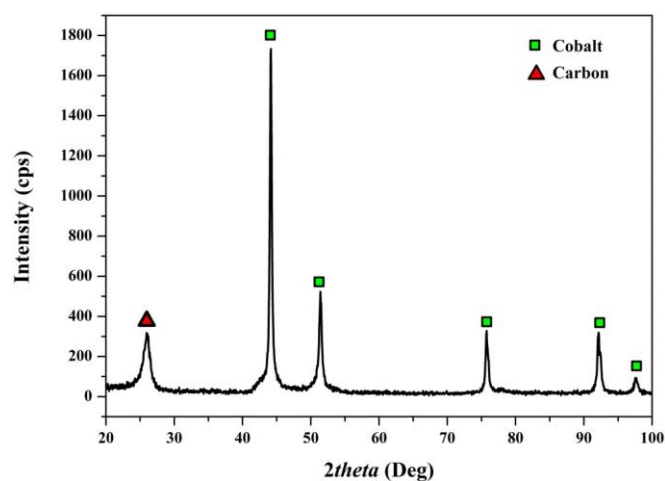

Fig. 1 XRD results for the prepared Cd-doped Co/C NPs

The obtained cobalt basic acetate here is relatively more stable, so it needs more heat to decompose. The third peak (at ~ 225 °C) can be assigned as the decomposition stage of this compound. As maximum weight loss is obtained at around 225 °C and according to the thermal decomposition

data of the pristine PVA[29], it is acceptable to say that this peak represents also the destruction of this polymer. The broad peak (at ~510 °C) can be assigned as decomposition of the synthesized cobalt carbonate into cobalt monoxide (Eq. 6). It is noteworthy that acetic acid is formed fue to acetates decomposition, this acide furthere decomposes into some gases including reducing ones (CO and H_2) [16], so the formed cobalt oxide is reduced to cobalt metal.
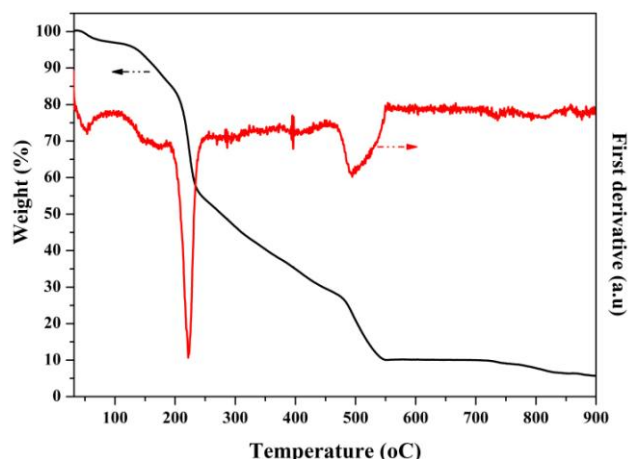
Fig. 2 Thermal gravimetry analysis (TGA) along with the first derivative for the CdAc/CoAc/PVA sol-gel
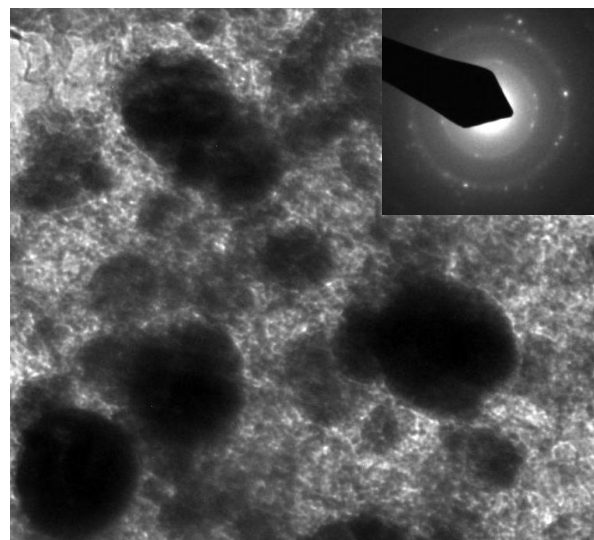

Fig.3 TEM image for the produced NPs. The inset represents SAED pattern

Fig. 3 displays the TEM images of the obtained powder. As shown in the figures, metallic nanoparticles surrounded by graphite shell are obtained. Moreover, from the sAED pattern (inset), one can claim that the metallic nanoparticles have a good crystallinity. Enveloping the cobalt nanostructures in graphite shell was introduced by the same authors [16].
Cyclic voltammetry (CV) is employed to evaluate the potential of the materials used for CDI and the specific capacitance can be calculated accordingly [17, 18]. Fig. 4-6

display the CV results for an electrode (typically, single electrode was used for all the measurement) made of the introduced nanoparticles at different NaCl concentrations; 0.1, 0.5 and 1M, and different scan rates; from 10 to 1000 mV/s. Although the introduced NPs have metallic substances, no Faradaic reactions are observed for the utilized electrodes, illustrating the ions are adsorbed on the electrodes surface by forming the electric double layer due to Coulombic interaction rather than electrochemical reactions [17]. The voltammograms are nearly rectangular within the applied potential ranges in which current quickly reached a plateau value after reversal of the potential sweep. An ideal capacitor would create a rectangular shape on a cyclic voltammogram [19]. The shape of the curves becomes more rectangular as the scan rate increases, while at the same time, the voltammetric currents increase. These imply that in the case of lower potential scan rates, the electrolytes have sufficient time to accumulate and arrange on the surface, which contributes greatly to the formation of double-layer capacitance[20]. Because of this, the electrosorption deionization becomes more efficient as the number of the absorbed ions greatly increases which strongly enhances the desalination process [21].
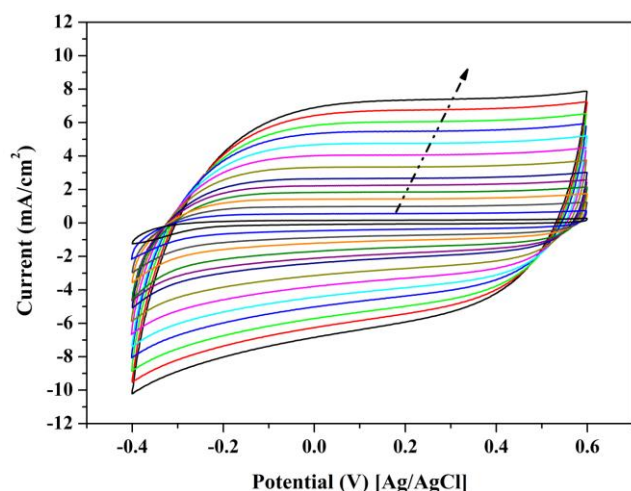
Fig. 4 Cyclic voltammetry results for the prepared Cd-doped Co/C electrodes at NaCl concentrations of 0.1 M; and scan rates; 10, 50, 100, 150, 200, 250, 300, 400, 500, 600, 700, 800, 900 and 1000 mV/s.

Capacitance is the ability of a body to store an electrical charge. Any object that can be electrically charged exhibits capacitance. In a parallel plate capacitor, capacitance is directly proportional to the surface area of the conductor plates and inversely proportional to the separation distance between the plates.There are similarities and differences in the test procedures for electrochemical capacitors and high power batteries. It is customary to perform constant current and constant power tests of both types of devices as well as pulse power tests.
From the constant current tests, the charge capacity (capacitance in Farads) and resistance of the devices are determined. We thus measured the specific capacitances of

introduced encapsulated and prepared graphene electrodes at the utilized scan rates. From the CV, the specific capacitance can be estimated as follow:

$$C = \frac{1}{vm} \int \frac{I}{V} dV \qquad (1)$$

Where C is the specific capacitance (F/g), v is the scan rate (V/s), m is the mass of the active material (g), I and V are the current density (A) and the corresponding voltage (V), respectively. In this study, numerical integration model was established to estimate the specific capacitance at every scan rate
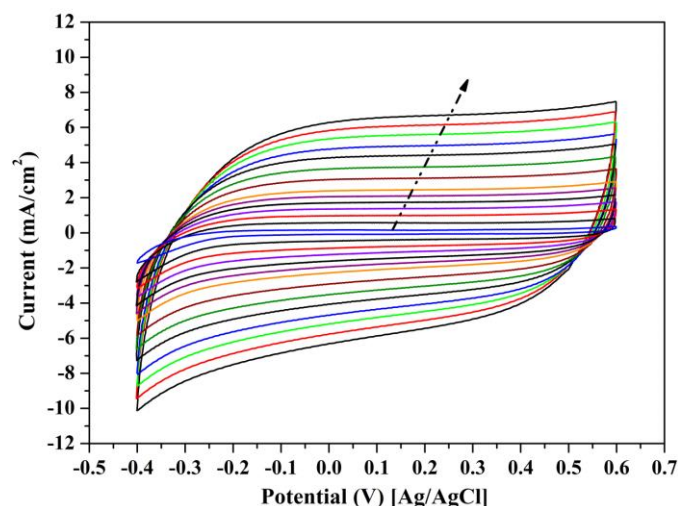
Fig. 5 Cyclic voltammetry results for the prepared Cd-doped Co/C electrodes at NaCl concentrations of 0.5 M; and scan rates; 10, 50, 100, 150, 200, 250, 300, 400, 500, 600, 700, 800, 900 and 1000 mV/s.
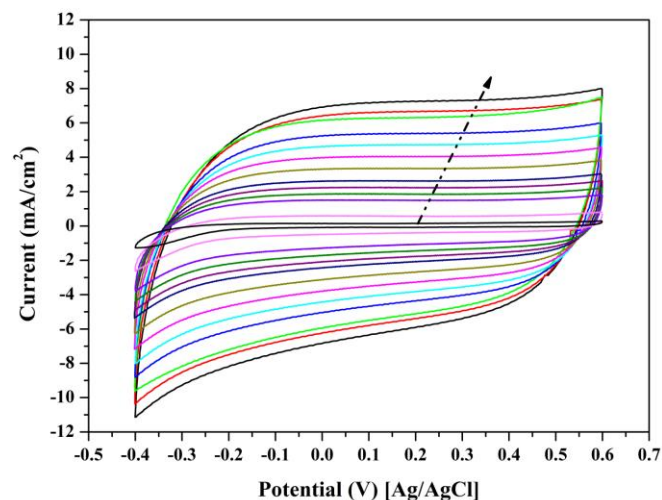
Fig. 6 Cyclic voltammetry results for the prepared Cd-doped Co/C electrodes at NaCl concentrations of 1.0 M; and scan rates; 10, 50, 100, 150, 200, 250, 300, 400, 500, 600, 700, 800, 900 and 1000 mV/s.
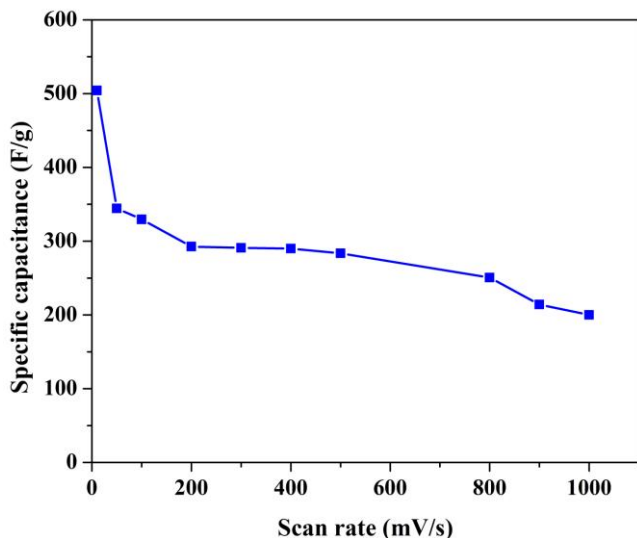
Fig. 7 Specific capacitance for the introduced Cd-doped Co/C NPs at different scan rates.

Fig. 7 represents the specific capacitance of the introduced nanoparticles in 1.0 NaCl solution at different scan rates. As shown in the figure, the introduced nanoparticles have high specific compared to many reported materials which concludes that these nanoparticles can be utilized as electrodes in the capacitive deionization technology. Moreover, the corresponding specific capacitance has acceptable stability at high scan rates which adds more advantages for the introduced nanoparticles.

Conclusion

Cadmium-doped cobalt nanoparticles encapsulated in a graphite shell can be prepared by calcination of a powder obtained from drying and grinding a sol-gel composed of cadmium acetate, cobalt acetate and poly(vinyl alcohol) in argon atmosphere at 700 ^{o}C. Due to the graphite shell, the introduced NPs can be utilized as effective electrode in the capacitive deionization instruments. Because of the bimetallic counterpart the introduced NPs behave good performance compared to many carbonaceous materials. The metallic constitute enhances the specific capacitance which has good reflection on the ions electrosorption process.

Acknowledgement

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