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ARTICLE TYPE

Binderless thin films of zeolite-templated carbon electrodes useful for electrochemical microcapacitors with ultrahigh rate performance

Ángel Berenguer-Murcia,^a Ramiro R. Ruiz-Rosas,^a Jaime García-Aguilar,^a Khanin Nueangnoraj,^b Hirotomo Nishihara,^b Emilia Morallón,^c Takashi Kyotani,^b and Diego Cazorla Amorós^{*a}⁵ Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

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Controlled nanozeolite deposits are prepared by electrochemical techniques on a macroporous carbon support and binderless thin film electrodes of zeolite-templated carbon are synthesized using the deposits as templates. The obtained film electrodes exhibit extremely high area capacitance (10–12 mF·cm⁻²) and an ultrahigh rate capability as a thin film capacitor.

15 Introduction

The development of materials for high performance supercapacitors has been the subject of intensive research since current portable electronic devices (e.g., smartphones) are reaching a point where their evergrowing functionality is limited by the existing technologies in energy management. The predominant energy storage mechanism in supercapacitors based on carbon electrodes is the formation of the electric double layer.¹ This kind of mechanism requires electrode materials that have the appropriate porous texture.² Porous carbon materials have been intensively investigated for the development of high performance supercapacitors, especially activated carbons^{3–5} and novel porous carbons whose porous texture may be fine-tuned depending on the preparation protocol.^{6–7} In this latter case, the solids known as zeolite templated carbons (ZTCs) stand out in the preparation of supercapacitor electrodes due to their exceptional textural properties.⁸ Nevertheless, these solids suffer from a critical drawback. Since these materials are prepared in the form of fine powders, preparation of the electrodes for supercapacitor applications requires shaping of the powders into continuous thin films with the highest packing density and good electrical conductivity. This step requires the use of a binder (e.g. fluorinated thermoplastics⁸ or more recently cellulose-based materials)⁹ and a carbon material with very small particle size such as acetylene black as conductivity promoter, to fabricate a stable electrode with a very thin cross-section to avoid mass transfer limitations. Binder materials, while conferring cohesion to the carbon particles, are insulators, and thus the prepared materials show very high interparticle resistance due to the polymer aggregates being located between the carbon particles. This ultimately results in the prepared electrodes showing very poor electrochemical behavior when submitted to fast charge-discharge rates, which makes the addition of the conductivity promoter necessary. Furthermore, these loads are frequently used

Broader context

Thin film capacitors (or microcapacitors) aim to fill a latent demand for the development of high efficiency energy supply and management systems. These must couple as high a capacitance as possible with a rate capability which is not diminished even when submitted to extreme specific currents. Recent reports published in the last few years have shown significant progress in this field, although the capacitances reported are not outstanding (0.5–3.4 mF·cm⁻²). In this communication, thin films of zeolite templated carbon are prepared on a carbon current collector by the combination of chemical and electrochemical synthesis protocols, giving rise to materials with exceptional properties that can be used as electrodes for microcapacitors, both in terms of rate performance and specific capacitance. This work has a great impact on the development of microcapacitor technology and should be of great interest for scientists working on energy storage, especially in miniaturized energy storage devices for applications such as portable electronic equipment or wireless sensor networks.

in concentrations between 10 and 20 %wt. in the final material, which is also a significant drawback. In recent years, the development of capacitors based on thin films (also known as microcapacitors) has opened a new research pathway for the development of high power density and energy density devices. This approach has been investigated from the perspective of Origami fabrication protocols,^{10a} printed materials,^{10b,10c} or by electrochemical techniques,^{10d} obtaining specific capacitance values for each electrode between 0.5 and 3.4 mF·cm⁻². The pivotal idea of this approach is that if a continuous thin film of a carbon material with the appropriate porous texture could be directly deposited on a suitable current collector without the use of binders or conductivity promoters, the synthesized devices would show very high rate performances and thus may be instrumental in the development of high energy and high power density systems.

Experimental

Benefitting from our experience in the preparation of controlled zeolite deposits by an electrophoretic deposition (EPD) technique from colloidal suspensions of MFI and LTA zeolites, we have prepared deposits of FAU nanozeolites (crystal size 25–60 nm) on

porous carbon discs following a procedure reported elsewhere^{11,12} (see Supplementary Information for full experimental details). The weight of the deposited layer of zeolitic material was always around 12 mg for all the experiments performed. Binderless continuous thin films of ZTC were synthesized by submitting the resulting composites to chemical vapour deposition (CVD) in an acetylene stream (15% in N₂) at 873 K for 4 hours followed by annealing of the resulting carbon-coated material at 1123 K for 3 hours. After HF washing, the composites were rinsed, dried, and characterized by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). In order to better compare our results, we also submitted the zeolite nanocrystalline powder to the same CVD conditions (see Supplementary Information).

Results and Discussion

The FE-SEM images of the zeolite layer supported on the macroporous carbon disc and its negative replica (layered ZTC) are shown in Figure 1.

Fig. 1 FE-SEM images of the (A) nanozeolite layer deposited by EPD on a current collector, and (B) ZTC layer obtained from the nanozeolite film after HF washing. Scale bars: 500 nm; Inset scale bar: 100 nm.

As Figs. 1 and S1 clearly show, the crystals size of the present FAU nanozeolites is very small, with sizes ranging from 25 to 60 nm, which is considerably smaller than those used in previous reports, in which zeolite crystals with size between 200 and 400 nm were used.⁸ Larger crystals (of approximately 100 nm in size and of cubic morphology) of zeolite LTA could also be observed. This was further confirmed by XRD and the contamination of the FAU zeolite phase was estimated to be low by analyzing the relative intensities of the characteristic peaks for each zeolite.

Fig. 3 (A, B) Cyclic voltammograms obtained for (A) the powder ZTC sample and (B) the binderless ZTC layer. Solid and dashed lines corresponds to scan rates of 100 and 5000 mV·s⁻¹, respectively. The voltammogram (100 mV·s⁻¹) for the blank macroporous carbon disc used as current collector is also shown by the dotted line in (B). (C) Galvanostatic charge-discharge curves for the binderless ZTC sample (full squares) and the carbon current collector (hollow circles) using a specific current of 70 mA·cm⁻². For an estimated ZTC weight of 40 µg (see below) the resulting specific current would be 1000 A·g⁻¹. A magnified view of the curve for the current collector is shown in Figure S6 (D) Capacitance retention vs. specific current plot for the binderless ZTC sample (solid line) and the powder ZTC sample (dashed line). Note: The secondary axis in Figure 3(D) applies only to the binderless ZTC sample.

The cyclic voltammogram of the powdered sample obtained at a low scan rate of 2 mV·s⁻¹ (Figure S6(A)) has the typical shape for ZTCs in sulfuric acid.¹⁴ At low scan rates, the ZTC electrode shows a very large capacitance owing to a large double-layer capacitance and redox processes at around 0.35 V (vs. Ag/AgCl) as a result of the surface functionality of the ZTC electrode in these experimental conditions. However, at a higher scan rate of 100 mV·s⁻¹ (Figure 3A), the shape of the voltammogram noticeably distorted due to the interparticle resistance in the case of the powder sample, indicating that the formation of double-layer is greatly restricted. In addition, the unique redox peaks in ZTC almost disappear. At a further high scan rate of 5000 mV·s⁻¹, almost no capacitance is obtained. These results clearly point out the limit of the rate capability in the powder ZTC, despite its superior rate performance compared to conventional activated carbons.¹⁵ This behavior greatly hinders the application of this type of powdered materials at ultrahigh rates, as other authors

Figure 1 also shows that the crystalline morphology of the zeolitic template is well replicated in ZTC, as reported previously.¹³ In order to verify that the zeolitic structure has been replicated at the nanometer level and that the formation of the ZTC has been successful, the prepared materials were analyzed by TEM. Figure 2 shows the obtained results.

Fig. 2 TEM images of (A) nanozeolite and (B) ZTC. These samples were taken scratched off the layers before observation. Inset scale bars: 20 nm.

From the TEM images it is clear that the ordering (or regularity) of (111) planes of zeolite FAU is replicated at the nanometer level, as evidenced by the lattice fringes of the individual ZTC crystals shown in the insets of Fig. 2B and in Figure S2. The observation of the lattice fringes in the ZTC crystals of the binderless layer (Fig 2B) is not so clear because of the deposition of a small amount of pyrolytic carbon on the surface. The ZTC samples presented in this study include both a sample directly deposited on a current collector in the form of a thin film without the use of a binder species and a powdered ZTC sample obtained from the nanozeolite powder which showed the characteristic XRD spectrum for ZTC materials (Figure S3) and an apparent surface area of 1250 m²·g⁻¹ obtained from its N₂ adsorption isotherm at 77K (Figure S4). It should be noted that even though in both materials the crystalline morphology was retained, the sample observed in the ZTC film showed a rough surface (inset in Figure 1B) compared to the material from the nanozeolite powder (Figure S1B). These two ZTCs having different bulk morphologies showed contrasting electrochemical behavior. Figure 3 shows the electrochemical characterization results obtained for both samples under different conditions (cyclic voltammetry and galvanostatic charge-discharge cycling).

have reported.⁸ However, it can be observed that the voltammogram obtained with the thin layer of ZTC maintains the rectangular shape of the voltammogram together with clear peaks of quinone/hydroquinone redox couple,¹⁶ even at 100 mV·s⁻¹. Considering a quite small contribution of the current corrector disc (dotted line in Figure 3B), such a high-rate capability is apparently owing to the ZTC layer. It is noteworthy that the quinone/hydroquinone redox reaction clearly takes place even at a high scan rate, only in the layered ZTC. It is generally anticipated that redox reaction is a relatively time-consuming process because of a charge-transfer resistance; however, Fig. 3A and 3B indicate the almost negligible effect of the charge-transfer resistance compared to inter-particle resistance, at least in ZTC. Thus, the formation of the binderless layer is very beneficial for ZTC to let its intrinsic performance be retained up to ultra-high rate process. Surprisingly, the formation of double-layer capacitance could be still confirmed at an ultra-high scan rate of

10000 mV·s⁻¹ (Figure S6(B)), in contrast to the case of the powder ZTC. From the cyclic voltammogram at a 5 mV·s⁻¹ and assuming that the capacitance of the ZTC layer deposited on the carbon disc was similar to that of the powder sample, the amount of ZTC was estimated to be ≈40 μg (this is about 70 μg·cm⁻², which would correspond to a specific current of 1000 A·g⁻¹). In this respect, it must be noted that the thickness of the synthesized ZTC layer could not be determined by FEG-SEM or HR-TEM, which is a clear indicative that the thickness was significantly below that of the deposited zeolite layer. It is remarkable that our results not only show the high rate performance of our materials, but also the obtained capacitance values (10–12 mF·cm⁻²) for the prepared electrodes under the same scan rates are at least 4 times higher than those reported in the literature for systems prepared using electrodeposited onion-like carbon particles on significantly more complex current collectors^{10d} by inkjet printing of carbon materials,^{10b,10c} or by electrochemical generation of mesoporous metal oxides on metal substrates,¹⁷ thus clearly outperforming them, even when submitting our samples to estimated specific currents of 1000 A·g⁻¹. The extreme rate performance of our binderless ZTC layer is further evidenced by the negligible ohmic drop observed in the charge-discharge experiments (Figure 3C) which maintains its triangular shape at high currents (70 mA·cm⁻²). It must be noted that the ohmic drop observed in the figure was solely due to the electrochemical set-up itself including the macroporous carbon support used as current collector and the mass transfer resistance of the electrolyte (See Supplementary Information). Furthermore, the outstanding capacitance retention in our material is evidenced by the loss of only 19% of its initial capacitance when submitting the binderless ZTC sample to a specific current of mA·cm⁻² (Figure 3D), which further serves to establish the stability of the sample after having undergone a large battery of electrochemical experiments.

Conclusions

In conclusion, the preparation of thin films of binderless self-standing ZTC layers by a combination of electrochemically assisted depositions techniques together with conventional CVD using a commercially available current collector with full compatibility with a carbon layer renders a novel family of materials with very high rate performance thanks to the absence of any binder material between the ZTC particles, and being not necessary the addition of conductivity promoter, which can be useful for the design of microcapacitors. Furthermore, the prepared thin ZTC layers show area capacitance values over 12 mF·cm⁻², which are, to the best of our knowledge the highest reported values to date for electrodes in microcapacitors. These novel solids and preparation methods should be regarded as highly interesting in the development of high energy density and high power density systems.

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Notes and references

- ⁶⁰ *Departamento de Química Inorgánica and Instituto Universitario de Materiales, Universidad de Alicante, Campus de San Vicente del Raspeig, Ap. 99, 03080 Alicante (Spain). Fax: +34 965903454; Tel: +34 965909350; E-mail: cazorla@ua.es*
- ⁶¹ *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1, Katahira, Sendai, 980-8577 (Japan). Fax: +81 222175626; Tel: +81 222175627; E-mail: kyotani@tagen.tohoku.ac.jp*
- ⁶² *Departamento de Química Física and Instituto Universitario de Materiales, Universidad de Alicante, Campus de San Vicente del Raspeig, Ap. 99, 03080 Alicante (Spain). Fax: +34 965903454; Tel: +34 965909820; E-mail: morallon@ua.es*
- † Electronic Supplementary Information (ESI) available: Details on the experimental procedure followed for the preparation of the nanozeolite crystals, their electrophoretic deposition on the carbon current collectors, as well as the detailed chemical vapour deposition applied may be found in the Supplementary Information. Full details on the carrying out of the electrochemical tests, as well as a detailed analysis of the ZTC sample prepared from the zeolite powder may also be found in the ESI, including TG analysis, SEM, TEM, XRD, and N₂ adsorption analysis. See DOI: 10.1039/b000000x/
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Graphical abstract

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