

Cycling characteristics of high energy density, electrochemically activated porous-carbon supercapacitor electrodes in aqueous electrolytes

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Carbon-based supercapacitors typically have low energy density but high cycle lifetime relative to batteries. Surface functionalization can significantly increase charge storage through reversible faradaic reactions at the electrode/electrolyte interface, a phenomenon known as pseudocapacitance. However, pseudocapacitive reactions, if not completely reversible, can contribute to reduced cycling performance. In this letter, we describe an electrochemical activation procedure on porous carbon synthesized *via* pyrolysis of photoresist which yields high specific capacitance and energy density of $\sim 250 \text{ F cm}^{-3}$ and 35 mW h cm^{-3} . We also demonstrate that the choice of aqueous electrolyte has a significant effect on both overall capacitance and cycle lifetime, through a comparison of KCl and H_2SO_4 electrolytes. Cycling in acid electrolyte yields excellent capacitance retention of 97% after 10 000 cycles.

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Introduction

Supercapacitors have garnered increasing research attention due to their high power density and long cycle lifetime relative to batteries.^{1–6} The mechanism for energy storage in supercapacitors relies primarily on two phenomena, double layer charging at the electrode/electrolyte interface and reversible redox reactions at the electrode surface, also known as pseudocapacitance. To maximize the energy density available through both these means, the surface area of the supercapacitor electrode must be high. Hence, activated carbon is a commonly used material for supercapacitor electrode fabrication due to its good electrical conductivity and high porosity.^{1–8} In addition to its high area available for double-layer capacitance, activated carbon presents the additional benefit of being amenable to surface chemical modification. Proper functionalization of the carbon surface can yield additional storage capacity through pseudocapacitive redox reactions.^{4,6–8}

The overall energy and power densities of a supercapacitor depend not only on the electrode surface area, but also on the selection of electrolyte, which is typically either an aqueous or organic salt solution, or an ionic liquid.^{1,4,8} Use of an aqueous electrolyte limits the available voltage due to electrolyte breakdown, but typically results in higher capacitance and lower electrolyte ionic resistance.^{1,4,6,8} Aqueous electrolytes have the additional benefits of being inexpensive and environmentally benign. In pseudocapacitive supercapacitors, the selection of a particular aqueous salt may also be expected to have a significant impact on overall performance as well as cycle lifetime.

The electrochemical modification of carbon electrodes has been demonstrated both to improve their overall surface area and to introduce electroactive functional groups which can contribute to pseudocapacitance.^{9–11} This technique offers promise in increasing the overall specific capacitance of supercapacitor devices. However, as this technique modifies the carbon material's structure and chemical composition, the effects on long term performance must be determined. In this paper, we examine the lifetime cycling performance of an activated porous carbon electrode fabricated from pyrolyzed photoresist in KCl and H_2SO_4 electrolyte. This fabrication technique is chosen due to its inherent scalability, particularly for on-chip micro-supercapacitor applications.¹² The impact of electrolyte selection on lifetime performance will be presented and discussed.

Methods

The fabrication of the carbon film from a commercial photoresist (SPR-220-7.0) is detailed in a previous work.¹² Briefly, photoresist is spin coated onto a Si wafer and is subsequently pyrolyzed in a hot wall chemical vapor deposition (CVD) reactor (Thermo Scientific Lindberg Blue M) at 900°C in H_2/Ar ambient. The electrochemical activation is inspired by ref. 10 and 11 and is performed in $0.5 \text{ M H}_2\text{SO}_4$ solution which is deaerated with bubbling N_2 for at least 20 minutes prior to activation. A 1.9 V bias (*vs.* Ag/AgCl) is applied for 1 hour, followed by 25 minutes of reduction at -0.3 V .

The electrochemical behavior is probed *via* cyclic voltammetry (CV), galvanostatic charge/discharge testing, and AC impedance spectroscopy. For these measurements, a copper wire is attached to the film using conductive silver epoxy, and the epoxy and the wire are coated in a nonconducting polymer

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resist such that only the carbon film interacts with the electrolyte during testing. A galvanostat/potentiostat (AC Instruments, 660D Model) is used with a Pt wire counter electrode and a Ag/AgCl reference electrode. Testing is performed in two commonly reported aqueous electrolytes, KCl (3.5 M) and H₂SO₄ (0.5 M). Lifetime cycle tests are performed using repetitive CV scans at a scan rate of 100 mV s⁻¹. The carbon films are characterized chemically and morphologically *via* X-ray photoelectron spectroscopy (XPS, Omicron) and scanning electron microscopy (SEM), respectively.

Results and discussion

Film characterization

The pyrolysis of SPR-220 photoresist results in a porous carbon film with good capacitive properties without additional activation.¹² After activation, the upper portion of the film is electrochemically modified to exhibit a rougher, more porous morphology, as evident from cross-sectional SEM images (Fig. 1). The overall thickness decreases from 1.4 μm to 1.2 μm. A similar change in morphology after electrochemical activation has been previously reported on glassy carbon electrodes.¹⁰ Based on differential electrochemical mass spectrometry performed by Sullivan *et al.*, the primary reaction product during oxidation is CO₂, which arises from the electrochemical etching of the carbon film.¹⁰ This etching increases the overall surface area by increasing access to otherwise closed pores. In addition to increasing the film porosity, this process also leads to the formation of oxygen-containing surface functional groups, as is apparent from XPS (Fig. 2). Following activation, the C 1s XPS peak clearly shifts and develops a high energy shoulder which can be attributed to the presence of oxygen-containing

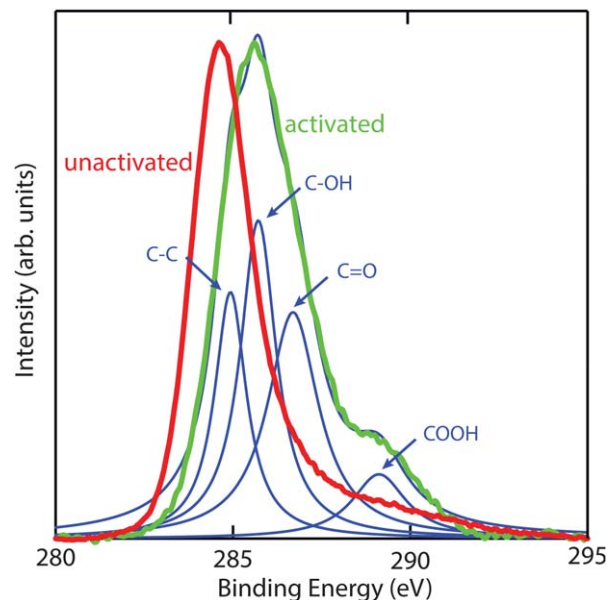


Fig. 2 C 1s X-ray photoelectron spectra of pyrolyzed photoresist before and after activation. Peak deconvolution is shown for activated film.

functionalities. The spectra shown in Fig. 2 were obtained using a Shirley background subtraction and fitted with Lorentzian peaks. Comparison of the C 1s and O 1s peak intensities reveals that the O : C ratio at the film surface increases from 12% before activation to 71% after activation. Both the increased surface area for double layer charging and the introduction of pseudo-capacitive surface functional groups are expected to contribute to an increase in the overall capacitance of the film. In addition, improved film and pore wetting has been observed in previous activation experiments, and may further contribute to increased capacitance through increased active surface area.⁸ While additional characterization of the film porosity (*e.g.* BET analysis) and surface chemistry (*e.g.* Boehm titration) is of great interest, the amount of material is insufficient to yield reliable adsorption or titration data, and is an area of ongoing investigation.

Galvanostatic charge/discharge

The effect of electrochemical activation on the galvanostatic charge/discharge behaviour in KCl is summarized in Fig. 3. While the unactivated film discharges in about 2.7 s at a constant current of 1 mA cm⁻², the same current density fully discharges the activated film in 42 s, demonstrating the higher overall energy density of the activated film. These discharge times correspond to specific capacitances of 2.7 mF cm⁻² before activation and 42 mF cm⁻² after activation, calculated *via* eqn (1):

$$C = \frac{I}{\Delta V / \Delta t} \quad (1)$$

where I is the discharge current density in A cm⁻² and $\Delta V / \Delta t$ is the average discharge rate in V s⁻¹. An extremely small IR drop is seen in both cases, indicative of a low equivalent series resistance (ESR), a key consideration for high power applications. Minimal

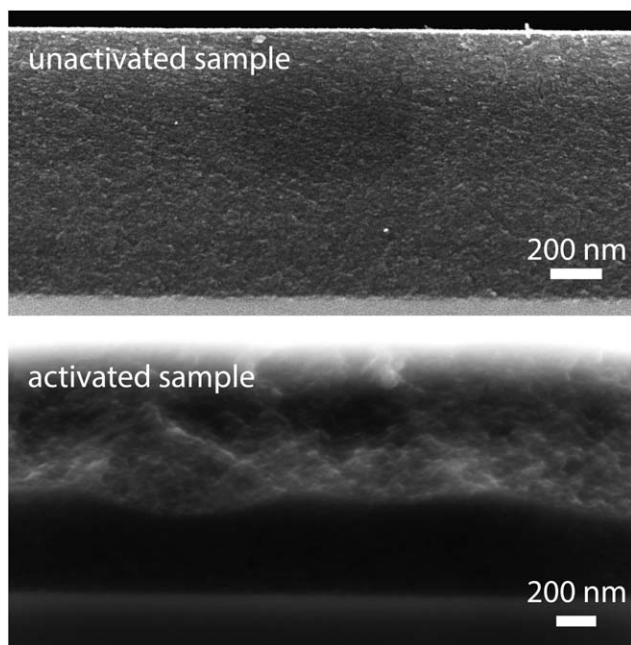


Fig. 1 Cross-sectional SEM images of pyrolyzed photoresist film before and after activation.

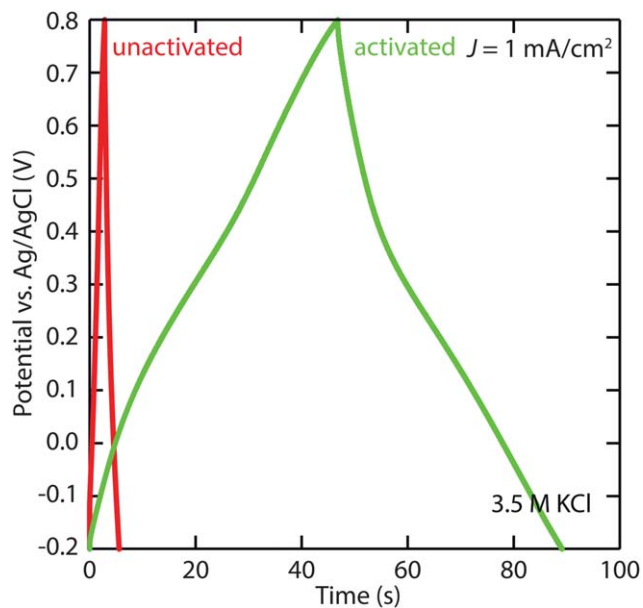


Fig. 3 Galvanostatic charge/discharge curves for activated and unactivated pyrolyzed photoresist film. Electrolyte is 3.5 M KCl. Current density is 1 mA cm^{-2} .

change in film ESR is seen after activation ($\sim 20 \Omega \text{ cm}^2$ before and after activation), indicating that any loss of film conductivity through oxidation is compensated by improved ion transport. The nonlinear shape of the discharge curve is indicative of the capacitive contribution of faradaic redox reactions.²

Cyclic voltammetry

CV sweeps confirm the improved capacitive performance of the electrochemically activated film. Fig. 4 shows the CV results

before and after activation, as measured in KCl and H_2SO_4 electrolytes at a scan rate of 100 mV s^{-1} . In both electrolytes, the activated sample shows significantly higher current density than the as-pyrolyzed sample. The specific capacitance is calculated from the CV results *via* eqn (1) where the average current density for the positive and negative sweeps is used for I . The specific areal capacitance calculated for the activated film as measured in H_2SO_4 is 30 mF cm^{-2} at a scan rate of 100 mV s^{-1} , revealing a $30\times$ increase with respect to the unactivated sample. The corresponding specific volumetric capacitance and energy density are $\sim 250 \text{ F cm}^{-3}$ and 35 mW h cm^{-3} . The calculated areal capacitance as measured in KCl is 24 mF cm^{-2} . These values are in good agreement with those obtained from charge/discharge tests.

In comparison to carbon-based electrodes which rely primarily on double-layer capacitance (and not pseudocapacitance), such as graphene/carbon nanotube carpets,¹³ onion-like carbon,¹⁴ and laser-scribed graphene,¹⁵ the areal capacitance achieved in this work is larger by an order of magnitude, demonstrating the higher energy storage capabilities of pseudocapacitive electrodes. The capacitance values also compare favorably to other pseudocapacitive carbon microsupercapacitors as in ref. 11, where a similar pyrolysis and activation procedure is used to fabricate 3D microstructured supercapacitor electrodes from SU-8 photoresist. In their work, a nearly identical areal capacitance of 30 mF cm^{-2} was demonstrated for the same scan rate; however, due to the large overall thickness of the 3D microstructure, the achieved volumetric capacitance was $\sim 20 \text{ F cm}^{-3}$, an order of magnitude less than the value demonstrated in this work. This significant deviation likely arises from a difference in pyrolysis procedure as detailed in ref. 12.

Not only the magnitude of the current is changed in the CV curves through activation, but the shape is modified as well. Before activation, the CV curve is fairly rectangular, indicating

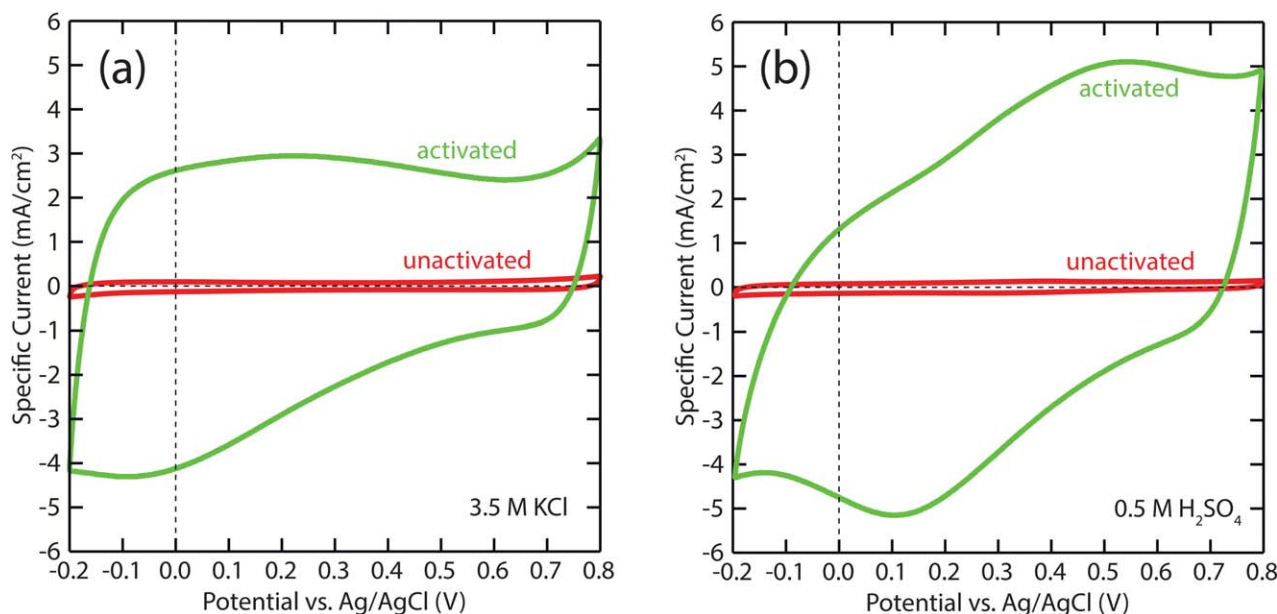
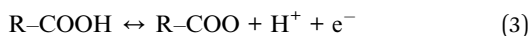
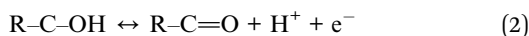


Fig. 4 Cyclic voltammetry comparison of activated and unactivated pyrolyzed carbon thin film electrodes. (a) CV performed in 3.5 M KCl electrolyte. (b) CV performed in 0.5 M H_2SO_4 electrolyte. Scan rate is 100 mV s^{-1} .

nearly ideal capacitive performance. After activation, on the other hand, large peaks are apparent, particularly when measured in the acidic solution, indicating the increased occurrence of faradaic reactions at the electrode surface. These redox reactions are well documented for carbon electrodes and have been attributed to reactions such as:^{7,16}



These oxygen-containing functional groups, which are formed during electrochemical activation, can be reversibly oxidized and reduced and can hence contribute to pseudocapacitance.

Comparison between KCl and H₂SO₄ electrolytes

Comparison of the CV curves after activation (shown in Fig. 4) as measured in the two electrolytes is also instructive: the shape of the CV curve as measured in H₂SO₄ shows a reversible character, with fairly symmetric oxidation and reduction peaks, whereas the measurement in KCl results in a broad reduction peak between -0.2 and 0.3 V without a corresponding oxidation peak of equal magnitude. This electrolyte dependence can be understood given the participation of hydronium ions in the proposed faradaic reactions. The Nernst equation, which governs the potential of a redox system, can be used to elucidate this phenomenon:

$$\Delta E = \frac{RT}{nF} \ln \frac{a_{\text{O}}}{a_{\text{R}}} \quad (4)$$

where ΔE is the shift in reduction potential, R the ideal gas constant, T the temperature, F the Faraday's constant, a_{O} the activity of the oxidant (H^+ in this case), a_{R} the activity of the reductant, and n the number of electrons transferred in the redox reaction. In this case, where the precise nature of the

reactions is uncertain, a rigorous quantitative analysis is difficult, but the trend of increasing reduction potential with increasing acidity is, nonetheless, qualitatively clear. Due to this shift in reduction potential in acidic solution, the reversible redox peaks can be clearly seen in the CV sweeps of the samples in 0.5 M H₂SO₄, but not in KCl, where the potential may remain outside the measurement window (further expansion of the CV window is not particularly instructive, as outside of this window, significant water oxidation and reduction begins to occur). Therefore, higher pseudocapacitance can be expected in acidic solutions in comparison to neutral electrolytes. A similar result was observed for voltammogram studies of activated carbon nanotube electrodes in NaCl and H₂SO₄ electrolytes.¹⁷ Galvanostatic charge/discharge tests show similar ESR values in both electrolytes, indicating similar power performances.

Lifetime comparison for cycling in KCl vs. H₂SO₄

The robust cycle lifetime of supercapacitors is a commonly cited advantage over battery alternatives.^{1,2} This robust performance stems from the purely electrostatic mechanism of charge storage in double-layer capacitors. However, supercapacitors that rely primarily on pseudocapacitive charge storage vary in their cycle performance due to irreversibilities in their faradaic reactions.^{7,16} If the redox reactions that contribute to pseudocapacitance are not completely reversible, a gradual decrease in capacity can be expected. As discussed previously, the electrolyte used can have a significant impact on these phenomena, with the H₂SO₄ electrolyte resulting in a higher reversibility than the KCl electrolyte in the CV analysis. In order to further probe this effect, repetitive CV scans were conducted at a scan rate of 100 mV s⁻¹ in both KCl and H₂SO₄ solutions for the unactivated and activated samples. The capacitance change for each test is plotted in Fig. 5. For the activated samples (Fig. 5b), the lifetime test as performed in KCl

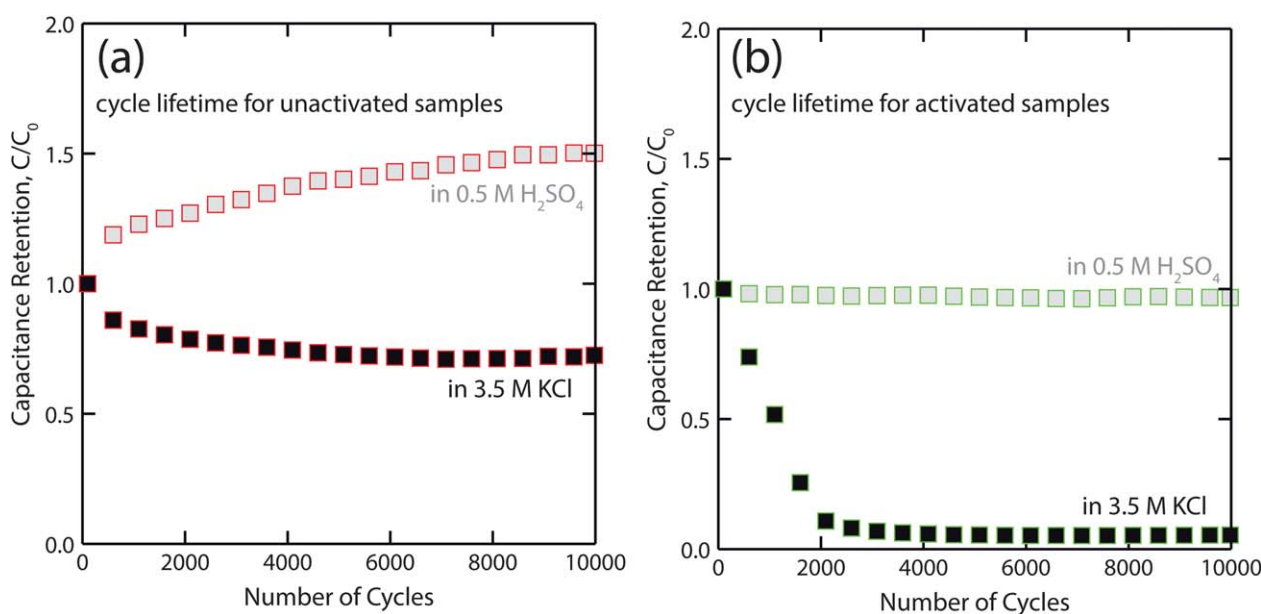


Fig. 5 Comparison of lifetime cycling tests in 3.5 M KCl and 0.5 M H₂SO₄ for (a) unactivated and (b) activated samples. Capacitance values are calculated from CV data.

shows rapid performance degradation over time, with a capacitance loss of nearly 95% after 10 000 cycles, as a result of the irreversibility of the faradaic redox reactions. This result was confirmed using a 10 000 cycle galvanostatic charge/discharge test, which yielded a similar performance degradation. Superior reversibility in the H_2SO_4 electrolyte results in significantly improved performance stability, which shows a capacitance loss of only 3%. For the unactivated samples, the test in KCl shows good stability, as has been previously reported,¹² while the test in H_2SO_4 actually shows an increase in capacitance over 10 000 cycles. KOH is another commonly employed electrolyte but in the present study and for the proposed on-chip applications, its use is impractical due to the well-known etching of the Si substrate in KOH.¹⁸

In order to probe the sources of the variance in lifetime performance for the activated and unactivated samples in various electrolytes, it is instructive to investigate the progression of the CV shape over the lifetime test. Fig. 6 shows a superimposition of all 10 000 CV cycles. The observed behavior varies significantly depending on both the electrode and the electrolyte. In the case of lifetime cycling in 3.5 M KCl (Fig. 6a and

b), the current magnitude, and hence the capacitance, decreases for both the unactivated and activated samples, indicating either that the area for double layer charging is decreasing with cycling or that the pseudocapacitive contribution to capacitance is decreasing. Given the more significant decrease in capacitance for the electrochemically activated sample, the latter explanation is likely the primary contributor to the reduction in performance with cycling. As previously discussed, the irreversibility of faradaic reactions in KCl likely results in decreasing pseudocapacitance over many cycles. In contrast, the CV shape and size for the activated sample in H_2SO_4 is remarkably consistent over the duration of the test (Fig. 6d). Hence, for the electrochemically activated films, the use of an acidic electrolyte not only improves the overall capacitance, but also the cycle lifetime performance due to the contribution of reversible faradaic reactions to pseudocapacitance. For the unactivated samples, the sample in H_2SO_4 is apparently being activated during the test itself through the repeated oxidation and reduction cycles (Fig. 6c). An increase in the current can be clearly seen throughout the progression the lifetime test, and the shape of the CV curve after 10 000 cycles resembles that of the electrochemically activated samples. Since

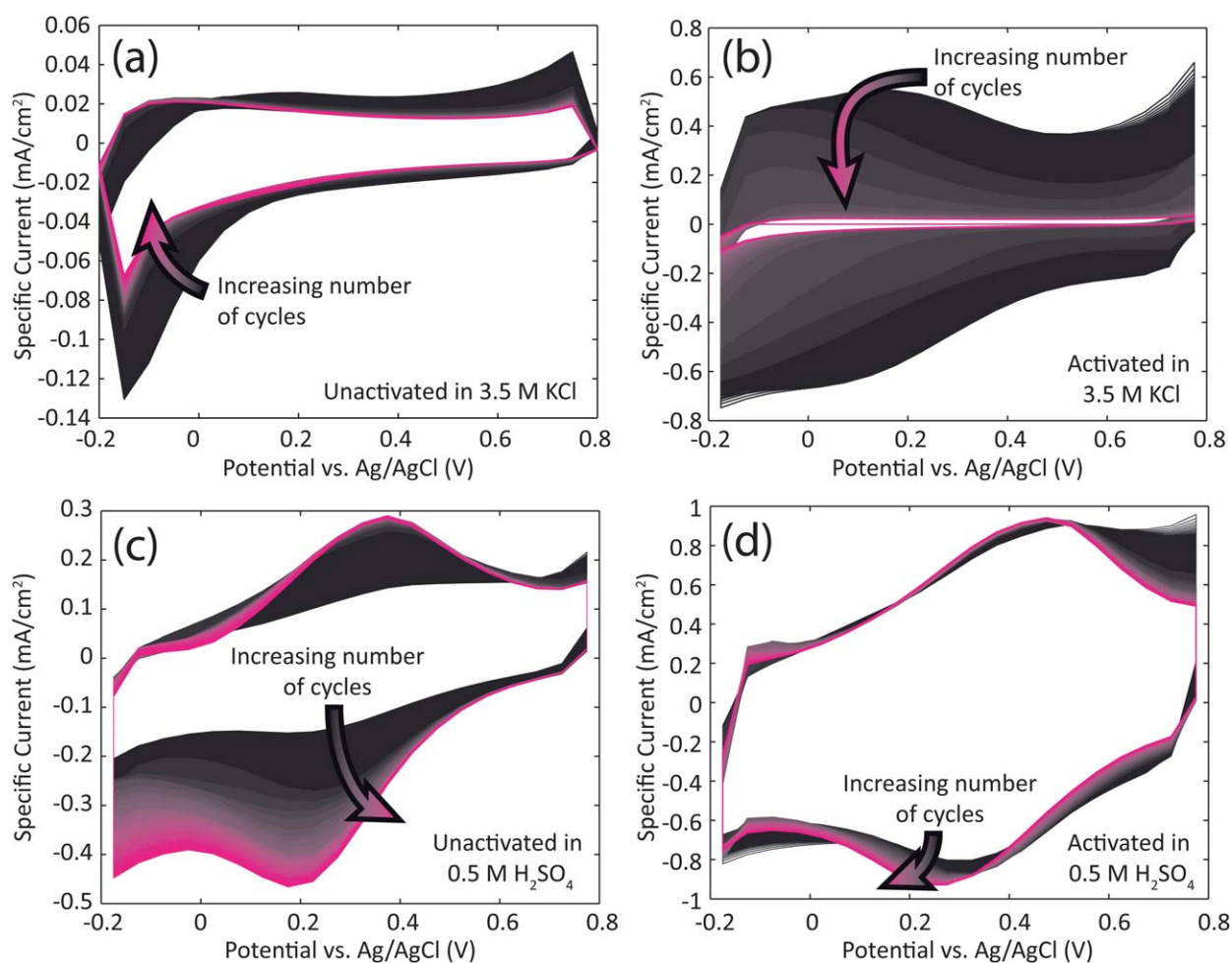


Fig. 6 The evolution of cyclic voltammograms over 10 000 cycles scanned at 100 mV s^{-1} for (a) an unactivated electrode cycled in 3.5 M KCl, (b) an activated electrode cycled in 3.5 M KCl, (c) an unactivated electrode cycled in 0.5 M H_2SO_4 , (d) an activated electrode cycled in 0.5 M H_2SO_4 . The arrows show the direction of increasing cycles.

the voltages used in the lifetime cycling are less than those used in the electrochemical activation step, the increase in overall capacitance after cycling is not large (a 50% increase in capacitance over 10 000 cycles), but the behavior is nonetheless similar.

Conclusion

In summary, the electrochemical activation of photoresist-derived porous carbon electrodes can yield significantly improved capacitance, but selection of an operating electrolyte is crucial to long term robust performance. A 0.5 M H₂SO₄ medium results in highly improved capacitance as well as lifetime cyclability relative to a 3.5 M KCl solution. This finding may hold true for other activated carbon electrolyte materials including carbon nanotubes and graphene oxide which rely on pseudocapacitive redox reactions, and is a focus of future investigation. The careful consideration of electrolyte and its impact on the long term performance of pseudocapacitive supercapacitors is crucial for the practical application of these types of energy storage devices.

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