Electrochemical characteristics of nano-graphene on a macroporous electrically conductive network prepared by hydrothermal carbonization

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ABSTRACT

Nano-graphene is fabricated on a macroporous electrical conductive network by hydrothermal carburization and subsequent annealing in Ar and the electrochemical characteristics are studied systematically in an alkaline electrolyte. The nano-graphene on the nickel particles improve the electrochemical properties of the three-dimensional (3D) electrode, especially the solution resistance, ion adsorption/desorption processes due to the large surface area and large surface defect concentration, as well as stability in the electrolyte. The novel 3D electrode has excellent electrochemical properties and large potential in energy storage and photoelectrochemical devices.

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1. Introduction

The merits of three dimensional (3D) structures with short transport lengths and high surface-to-volume ratios are more obvious as on-board power sources become increasingly smaller. The 3D architectures enable better utilization of space in energy storage devices enabling a smaller footprint while retaining large power and energy densities [1–6]. In 3D energy devices, the three-dimensional electrode is the basic and important component which affects the performance of the energy device. In this respect, the combination of rechargeable devices such as batteries and supercapacitors fabricated in a 3D architecture by microelectromechanical (MEMS) techniques is a good direction. Different kinds of 3D architectures such as interdigital structures, nanometer- or micrometer-sized wire arrays, and microchannel plates (MCP) can be fabricated on silicon by standard MEMS techniques [7–18].

In addition to the electrode architecture, the choice of the electrode materials is crucial. Carbon materials such as active carbon, fullerene, carbon nanotubes, and graphene have been extensively studied because of their potential applications in energy storage, solar cells, sensors, and catalysts [19–21]. Carbon-based electroactive materials with small size and abundant surface area provide large electroactive regions and short diffusion paths for efficient access by the electrolyte to the electrode. In particular, graphene, a single layer of carbon atoms arranged in a honeycomb lattice, has the desirable 2D structure boasting high electrical and thermal conductivity, mechanical strength, and large specific surface area [22]. Recently, 3D graphene structures have attracted increasing attention due to the high porosity and large specific area [23–25], and the 3D architecture based on graphene can be as a network to produce the pass channel for fast electron and ion transport. It is suitable for future applications in energy, catalysis, sensing, and biomedical engineering and science for 3D graphene structure due to its excellent electrochemical properties [26–28]. There are several approaches to convert 2D graphene into a 3D architecture, for example, by using a template, layer stacking, and chemical vapor deposition (CVD) [29,30]. For example, a 3D graphene foam can be synthesized by CVD using nickel foam as the porous template on which graphene is deposited by CVD followed by removal of the template to form the 3D graphene foam.
However, fabrication of 3D graphene foam is hindered by spontaneous agglomeration and restacking of the graphene nanosheets due to the large Van der Waals attraction between adjacent sheets [31]. Aggregation of graphene degrades the properties such as the specific surface area and ion transport.

3D Si architectures, such as Si microchannel plates (SiMCP), can be formed by standard MEMS techniques [32–34]. The SiMCP is a perforated through-hole substrate which can be formed by photo-assisted electro-chemical etching followed by electrochemical peeling from the Si substrate to form the free-standing stable layered structure. The SiMCP has a big area ratio (>70%) and aspect ratio (length/diameter of hole > 40 or more) and the surface area gain can be larger than 100. After electroless plating of nickel, the 3D macroporous electrically conductive network (MECN) is formed and it has good stability in alkaline media and can even be annealed at a high temperature in subsequent processing steps. Hence, the MECN has been employed to fabricate 3D nano-graphene by hydrothermal carbonization [35] and the structure delivers better performance pertaining to field emission and supercapacitance [36,37]. Such as, after the active material Co (OH)₂ deposited on the nano-graphene coated MECN, the 3D electrodes exhibit a fast electron and ion transport properties and demonstrate the excellent stability and durability. However, it is necessary to understand the electrochemical properties of the 3D graphene structure on MECN in order to provide insights into the fabrication of future high-performance 3D energy devices. In this work, the electrochemical properties of 3D nano-graphene prepared on MECN are studied systematically by electrochemical methods.

2. Experimental details

All the chemical reagents were analytical grade (AR) and used as received without further purification. Nickel chloride hexahydrate (NiCl₂·6H₂O) and ammonium chloride (NH₄Cl) were purchased from Aladdin Reagent and triethylene glycol (C₆H₄O₂), sodium hypophosphate monohydrate (NaH₂PO₂·H₂O), ethanol, and other reagents were bought from Sinopharm Chemical Reagent Co. Ltd. Deionized water was used throughout the experiments.

A p-type (100) silicon wafer with a thickness of 525 μm was used and the standard microelectronics fabrication steps were implemented to produce the SiMCP. The steps included thermal oxidation to produce a masking layer and 3 μm × 3 μm squares were patterned by lithography and wet etching. The patterned wafer was pre-etched in a tetramethyl ammonium hydroxide (TMAH) solution (25% at 85 °C) and anodized on a computer-controlled photo-assisted electrochemical system. More details about the process can be found in Refs. 33 and 34. The SiMCP was cut into 1 cm × 1 cm square pieces for further processing.

Electroless nickel plating was performed. The SiMCP was dipped in diluted HF for 30 s to remove the native oxide and soaked in a buffer solution (0.1% Triton X-100 solution) for 30 s to decrease the inner stress and enhance wetting prior to immersion in a plating bath for 20 min at 90 °C. The plating medium was prepared by dissolving 6 g of NiCl₂·6H₂O, 10 g of NH₄Cl, and 2 g of NaH₂PO₂·H₂O in 200 ml of deionized water to form a green mixture. An appropriate amount of NH₄OH was added to adjust the pH 8–10 and it was stirred for 30 min. The nickel–coated SiMCP (MECN) was taken out and rinsed with water again.

Sodium acetate trihydrate was dissolved in triethylene glycol [CH₂(COO)₂Na·3H₂O: C₆H₄O₂·Na·3H₂O = 1:10] and stirred magnetically for 30 minutes. The MECNs were introduced into the solution and sonicated for 5 minutes to fill the microchannels in the MECNs with the solution. The solution and MECNs were then transferred to a Teflon-sealed stainless steel autoclave, sealed tightly, inserted in a vacuum oven heated to 250 °C, and kept at that temperature for 1–8 hours to produce different samples of the carbon-nickel alloy (NiC)/Ni/SiMCPS (designated as NiC-MCP). The samples were cooled in the autoclave to room temperature, taken out, rinsed with deionized water for 10 minutes, and vacuum dried at 80 °C. Afterwards, the NiC-MCPs were placed in a tube furnace at 650 °C and annealed in argon for 1 hour to cover the inner channels and surface of the MECNs with a nano-graphene layer (labeled as NG-MCP).

The morphology and microstructure of the samples were examined by scanning electron microscopy (FE-SEM, Hitachi S-4800, Japan) and high-resolution transmission electron microscopy (HRTEM; Philips Tecnai G2 F30) and the crystal structure was determined by X-ray diffraction (XRD, Rigaku, RINT2000, Japan). The electromechanical tests were performed on a CHI660D electrochemical workstation (Shanghai Chenhua CHI660D) in the three-electrode mode in which the sample, platinum electrode, and saturated calomel electrode (SCE) served as the working electrode, counter electrode, and reference electrode respectively. The samples were exposed to 1 mol L⁻¹ KOH electrolyte at room temperature (25 °C). Cyclic voltammograms (CV) were acquired in the potential range between −1.2 and 0.6 V vs. SCE at different scanning rates from 10 to 150 mV s⁻¹. The Randles plots were obtained from the polarization tests conducted at sweep rates of 1 mV s⁻¹ in the anodic direction. The data in the Randles plots in the range of ±200 mV from the open circuit potential were selected to evaluate the corrosion behavior. Electrochemical impedance spectra (EIS) was performed in the frequency range from 1 to 10,000 Hz at the open circuit potential (OCP). In the Mott–Schottky analysis, the impedance-potential curves were obtained by sweeping the potential in the positive direction at an excitation voltage of 5 mV and frequencies from 1 to 1000 Hz. The data were normalized by the foot print area.

3. Results and discussion

The top and cross-sectional views of the SiMCP are shown in the SEM images in Fig. 1(a) and (b). The microchannels have a depth of around 200 μm and size of 5 × 5 μm giving an aspect ratio of the microchannels of about 40. After electroless nickel plating, the surface and side-wall of the SiMCPS are coated uniformly with a thin disordered nickel layer with thickness about 0.5 μm (Fig. 1c and d) composed of porous nickel grains with a size of about 50 nm. Since the porous nickel balls are deposited on the outer and inner surfaces of the SiMCP and the porosity of the Ni electrode, the surface area of the 3D nickel layer increases by almost 100 times [22].

Fig. 1e–h depict the top-view images of the 3D Ni-MCPs prepared for different hydrothermal time from 1 to 8 hours. The Ni-C alloy layer becomes thicker with time. When carbon is introduced to the Ni layer during hydrothermal carbonization, the thickness of the Ni-C layer increases from about 1 μm (1 h, Fig. 1e) to about 1.5 μm (3 h, Fig. 1f). The wall thickness of the Ni-C layer reaches about 2 and 2.5 μm after 6 and 8 h, respectively. Local preferential growth is observed because the thick silicon layer is retained in these regions during photo-assisted electrochemical etching to form the SiMCP (Fig. 1a), for example, at the cross points and middle of the wall. A large amount of Ni is deposited on the projection of silicon structure during electroless Ni plating (Fig. 1c). The thicker Ni layer can be inserted with more carbon during hydrothermal carbonization and the Ni-C layer can expand perpendicular to the channel direction or along the channel direction at the cross points and middle of the wall (Fig. 1e–h). After hydrothermal carbonization for 8 h, the cubic holes in the SiMCP with a length of 5 μm change to irregular channel and the side length decreases to about 2.5 μm due to expansion of the Ni-C
Fig. 1. SEM images: (a, b) Top-view and cross-sectional images of the silicon microchannel plate (SiMCP); (c, d) Macroporous electrically conductive network (MECN); Top-view images of NiC-MCPs after hydrothermal carbonization for (e) 1 h, (f) 3 h, (g) 6 h, and (h) 8 h.

layer (Fig. 1h). However, they still retain the original 3D structure because the morphology does not change at 250°C during hydrothermal carbonization. After annealing at 650°C for 1 hour, nanometer-sized balls are observed from the surface of the MECN hydrothermally carbonized for 3 h (Fig. 2a). In addition, many balls about 50 nm sizes emerge from on inner channel as shown by the cross-sectional SEM image in Fig. 2b. Fig. 2c shows that the sample contains carbon, oxygen, nickel and silicon and the mass and atom ratios of carbon to the other elements are 16.54% and 47.21%, respectively.

In order to obtain detailed structural information and morphology evolution of the NiC-MCPs and NG-MCPs, the TEM images and selected-area electron diffraction (SAED) patterns are presented in Fig. 2d–e. The NiC alloy with a lattice spacing of 0.24 nm can be found on the Ni layer with a lattice spacing is 0.2 nm (Fig. 2d). After post-annealing at 650°C for 1 hour, clear

Fig. 2. NG-MCPs after hydrothermal carbonization for 3 hours: (a) Top-view; (b) Cross-sectional SEM image; (c) EDS results; TEM images of (d) NiC/Ni and (e) Nano-graphene/Ni (inset: SAED pattern of transparent region); (f) XRD patterns of MECN, NiC-MCPs, and NG-MCPs.
graphitic layers with a 0.32 nm lattice spacing is formed on the Ni surface (Fig. 2e). The SAED pattern reveals six-fold symmetry diffraction dots illustrating the high crystalline quality of the nanographene. The results show that carbon atoms diffuse into the Ni layer to form Ni-C during hydrothermal carburization and then the carbon atoms diffuse from the Ni-C alloy to form the nanographene layer on the surface of nickel during post-annealing. The nickel layer is composed of particles with a nanometer size and the nanoballs with a diameter of about 50 nm are observed from the surface and inner wall of the MECNs (Fig. 2a–b) after post-annealing. During segregation of carbon from Ni-C, some Ni nanoballs may be exfoliated from the Ni-C alloy and the wall thickness is reduced correspondingly (Fig. 2a).

The X-ray diffraction (XRD) patterns in Fig. 2f illustrate the phase changes in MECN, Ni-C-MCPs and NG-MCPs during hydrothermal carburization. There are four peaks in the XRD image of the MECN. One peak can be attributed to the Si substrate ([400] peak at 28°=69.3°, marked with a solid diamond) and the other three peaks arise from the cubic phase Ni metal [JCPDS 70-1849, with the (111) peak at 28°=44.7°, (200) peak at 28°=52.1°, and (220) peak at 28°=76.6°, marked with a hollow diamond]. These prepared MECNs react with polyol to induce cleavage of the C–C bonds and the Ni-C alloy is formed with carbon diffusing into the Ni during hydrothermal carburization. The XRD peaks of hexagonal nickel carbide (Ni3C phase, marked with a circle) appear [JCPDS 77-0194, (212) peak at 28°=39.1°, (411) peak at 28°=41.6°, (312) peak at 28°=44.6°, (611) peak at 28°=58.4°, (433) peak at 28°=71.2°, (314) peak at 28°=78.1°] and the peak intensity increases while the cubic phase nickel peak intensity diminishes gradually as the hydrothermal time is increased. Carbon atoms penetrate the Ni nanoparticles forming the Ni3C phase. After annealing at 650 °C in Ar, all of the hexagonal Ni3C phase peaks disappear and a broad peak of graphite (002) (marked with a pentagram) appears at about 28°=25° along with the peaks of the cubic Ni phase. Indeed, the Raman data have been proved that high quality nano-graphene can be formed on MECN substrates at annealed temperature above 500 °C in Ar, which shows an apparently larger Raman peaks ID/IG ratio [36].

The cyclic voltammograms (CV) acquired from MECN, Ni-C-MCP, and NG-MCP in the potential range of 1.2–0.6 V vs. SCE at scanning rates between 10 and 100 mV s⁻¹ are shown in Fig. 3. Similar cyclic voltammograms and oxidation-reduction behavior are observed from these samples in this potential region. They are the typical oxidation-reduction reaction curves of Ni metal in KOH. During the first potential scan, the passive layer which consists of an amorphous α-Ni(OH)2 layer is formed as indicated by the current peak A1. When the potential is reversed, a reduction process is observed corresponding to the cathodic peak C1. In the potential domain of the plateau (B), the amount of nickel oxide increases and there is simultaneous transformation of α-Ni(OH)2 into less hydrated and crystallized β-Ni(OH)2. At a potential bigger than that of the oxidation peak A1, β-Ni(OH)2 is oxidized into β-NiOOH and the transformation is complete when the water oxidation current is observed. During the decreasing potential scan, the reverse reduction reaction from β-NiOOH to β-Ni(OH)2 is observed corresponding to the cathodic peak C2. However, there are some differences. First of all, the current densities of plateau B increase with the hydrothermal carburization time and the ratio of the peak current (IB/IB) increases from about 0.17 (MECN) to about 0.24 (Ni-C-MCP 3 and 6 h) and 0.28 for Ni-C-MCP 8 h. The Ni-C alloy is formed by the diffusion of carbon into the Ni-MCPs and the carbon constituents in the Ni-C layer transforms the α-Ni(OH)2 into crystallized β-Ni(OH)2. After post-annealing, carbon diffuses from the Ni-C alloy to form the nano-graphene. The transformation process of Ni(OH)2 is restrained and the current densities of plateau B decrease. Secondly, small peaks appear at the potential region from −0.8 to −0.2 V vs. SCE as shown the inset of cyclic voltammograms. The current density of the peaks increases with hydrothermal time corresponding to the oxidation-reduction behavior of Ni-C (peaks marked as A_{NiC} and C_{NiC}). After post-annealing, clear cathodic peaks emerge from −0.2 to −0.3 V vs. SCE and −0.3 to −0.5 V vs. SCE from the NG-MCP processed for 3 and 6 h, respectively. The small current density or integrated values of cathodic peaks means that the adsorption/desorption process can only occur in a few atomic layers on the surface of graphene-coated nickel particles [38,39]. However, as the hydrothermal time goes up, multi-layered graphene is formed on the nickel particles to improve adsorption/desorption as shown by the sample treated for 6 h (Fig. 3f and inset).

The cyclic voltammograms show how the current density (j, in the unit of A cm⁻²) changes with the scanning rate v (V s⁻¹) as shown in the plot of log (j) versus log (v) in Fig. 3g. All the samples show the cathodic peaks of Ni (A2) and the solid lines with slopes of 0.5 and 1 are shown for comparison. With regard to the MECN electrode, the current densities of the cathodic peaks increase with a slope of 0.75 at small scanning rates and then the slope approaches 0.5 for fast scanning rates. The high ohmic contribution of the metal layer limits the rate capability (only slope of 0.75) at the small scanning rates for the MECN with the 3D architecture [35]. When carbon diffuses into Ni (Ni-C-MCP 3 h), carbon atoms in limited quantities only stay on the surface of the Ni particles and the Ni-C alloy cannot be detected by XRD (Fig. 2f). In this case, the current density of the cathodic peaks increases with a slope of 1 at small scan rates and the electrochemical redox reaction is surface-controlled [39]. As more carbon atoms diffuse into the Ni layer, thick Ni-C is formed on the Ni particles (Ni-C-MCP 6 h and 8 h). The increasing current densities of the cathodic peaks indicate that surface carbon improves the electrochemical redox reaction of nickel in KOH. However, owing to the large ohmic contribution of the alloy layer which influences surface capacitive charging, the current densities of the cathodic peaks can only increase with a slope of 0.75 at small scanning rates. In all the samples, on account of the large surface area of the 3D architecture, the current densities of the cathodic peaks are controlled by semi-infinite linear diffusion and the slope approaches 0.5 for scanning rates larger than 50 mV s⁻¹. After post-annealing in Ar, nano-graphene is formed on the Ni particles. The current densities of the cathodic peaks increase with a slope of 1 for NG-MCP 3 h, indicating that the nano-graphene improves capacitive charging and the electrochemical redox reaction of nickel in KOH solution is surface-controlled thus showing the linear dependence in the current density versus scanning rate with a slope of 1. As more nano-graphene forms on the Ni particles (NG-MCP 6 h), the electrochemical redox reaction of nickel in KOH solution is improved leading to the increasing current densities of the cathodic peaks. However, the influence of surface capacitive charging decreases and the linear dependence of the current density versus scanning rate has a slope of 0.75.

In order to systematically study the electrochemical characteristics of the nano-graphene on MECN, electrochemical impedance spectra (EIS) are acquired in the frequency range from 0.1 to 100,000 Hz with a potential amplitude of 5 mV at the open-circuit potential (OCP). The impedance diagrams are shown in Fig. 4a and b as plots of Nyquist and Bode planes. The inset of Fig. 4a depicts the high-frequency domain. The schematic representation of the interface/electrolyte interfaces of the nickel electrode and corresponding equivalent electrical circuits (EC) are shown in Fig. 4c. The experimental (dotted) and fitted (line) data are shown after complex nonlinear least square (CNLS) fitting and the fitting parameters are listed in Table 1. With regard to MECN, the nickel layer on the surface of SIMCP is composed of 50 nm particles (Fig. 1c and d) and the schematic representation of the interface/
Fig. 3. Cyclic voltammograms in the potential range between –1.2 and 0.6 V vs. SCE at scanning rates from 10 to 100 mV/s: (a) MECN and NiC-MCPs hydrothermal processed for (b) 3 h, (c) 6 h, and (d) 8 h; NG-MCPs hydrothermal processed for (e) 3 h and (f) 6 h. The insets are the partial curves indicating the cathode peaks of carbon. (g) Log(j) versus log(v) for the cathodic peaks C2. The solid lines with slopes of 0.5 and 1 are shown for comparison.
RS is equivalent to CPE1 results for circuits as shown in the equation $Z_{CPE}$.

Table 1: Electrochemical test data.

<table>
<thead>
<tr>
<th>Samples</th>
<th>MECN</th>
<th>NiC-MCP 3h</th>
<th>NiC-MCP 6h</th>
<th>NiC-MCP 8h</th>
<th>NG-MCP 3h</th>
<th>NG-MCP 6h</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_S$</td>
<td>4.44</td>
<td>2.595</td>
<td>4.43</td>
<td>0.75</td>
<td>4.57</td>
<td>3.195</td>
</tr>
<tr>
<td>$R_I$</td>
<td>2.91</td>
<td>9.94</td>
<td>1082</td>
<td>1.838</td>
<td>14.1</td>
<td>7.0</td>
</tr>
<tr>
<td>CPE1-T</td>
<td>2.75E-3</td>
<td>2.3E-2</td>
<td>1.3E-3</td>
<td>5.67E-6</td>
<td>1.16E-3</td>
<td>1.4E-2</td>
</tr>
<tr>
<td>CPE1-P</td>
<td>0.77</td>
<td>0.78</td>
<td>0.91</td>
<td>0.85</td>
<td>0.87</td>
<td>0.74</td>
</tr>
<tr>
<td>$R_2$</td>
<td>952.7</td>
<td>278.3</td>
<td>1.01</td>
<td>0.8</td>
<td>2739</td>
<td>76.2</td>
</tr>
<tr>
<td>$C_2$</td>
<td>5.46E-4</td>
<td>4.2E-3</td>
<td>5.5E-4</td>
<td>1.2E-3</td>
<td>2.9E-4</td>
<td>2.3E-3</td>
</tr>
<tr>
<td>CPE2-T</td>
<td>1.44E-1</td>
<td>1.5E-2</td>
<td>5.5E-2</td>
<td>5.7E-3</td>
<td>2.05E-3</td>
<td>3.8E-3</td>
</tr>
<tr>
<td>CPE2-P</td>
<td>0.75</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.75</td>
<td>0.89</td>
</tr>
<tr>
<td>$V_p$</td>
<td>-0.503</td>
<td>-0.274</td>
<td>-0.123</td>
<td>-0.459</td>
<td>-0.182</td>
<td>-0.283</td>
</tr>
<tr>
<td>$I_{corr}$</td>
<td>2.2E-04</td>
<td>6.79E-05</td>
<td>2.72E-05</td>
<td>6.51E-04</td>
<td>5.55E-05</td>
<td>4.72E-05</td>
</tr>
<tr>
<td>$V_{fb}$</td>
<td>-0.07</td>
<td>-0.122</td>
<td>-0.134</td>
<td>0.01</td>
<td>0.322</td>
<td>0.268</td>
</tr>
<tr>
<td>$N_A$</td>
<td>2.02E21</td>
<td>1.29E22</td>
<td>2.33E21</td>
<td>9.91E21</td>
<td>2.67E21</td>
<td>7.44E21</td>
</tr>
</tbody>
</table>

where CPE-P and CPE-T are fitting parameters. When CPE-P is between 0 and 0.5, CPE tends to show the resistance characteristics but if CPE-P is between 0.5 and 1, it tends to show the capacitance characteristics. The parallel parameters of $C_2$ and $R_2$ represent the electrochemical process of the Ni layer in KOH solution and another constant phase element CPE2 is introduced to replace the Warburg impedance due to the influence of the 3D architecture of SiMCPs on mass transport. EC1 can also be used to represent the electrochemical process at the interface/electrolyte interface of...
NG-MCP and the nano-graphene coated nanosize Ni particles are shown in Fig. 2a and b. For NiC-MCPs, the Ni-C alloy is formed on the Ni layer (Fig. 1e–h) and the equivalent circuit EC2 represents the electrochemical process at the interface/electrolyte interface of NiC-MCPs. In the equivalent circuit, the parallel parameters of CPE1 and R1 represent the electrochemical process of the Ni-C layer in KOH solution and the other symbols have the same meaning as EC1. The small discrepancy between the experimental and fitted data at high frequencies may arise from the 3D architecture. That is, it is insufficient to represent the electrochemical process of the 3D electrode using the simple parallel parameters of CPE1 and R1 due to the distribution effects and porosity [42]. However, there is good consistency between the experimental and fitted data in the appropriate interface physical pictures and equivalent circuits. The corresponding fitted parameters can also show the physical meanings. The interface resistance between the electrode and solution decreases due to the larger surface area in the diffusion process of carbon into the nickel layer. The stability of the electrode increase in KOH, especially the nanosized particles, corresponding to increasing R1 and increasing index CPE1-P. That is to say, the small amount of carbon atoms diffusing into nickel to form Ni-C alloy protects the nickel layer from etching by KOH such as the case of NiC-MCP 3 h and 6 h. However, a large amount of carbon atoms expand the nickel layer (Fig. 1h) decreasing the stability of the nickel layer as in the case of NiC-MCP 8 h. The semi-circle in the high-frequency region (Fig. 4a inset) corresponds to the electrochemical redox reaction at the electrode surface. After post-annealing, the electrodes are stable in KOH as shown by the larger resistance values (R1 and R2) and the index of CPE-P parameters because nanographene is formed on the Ni particles.

The Tafel plots obtained in 1 mol L−1 KOH are shown in Fig. 4d and the corrosion data are listed in Table 1. The corrosion current density (i corr) and polarization potential (V p) are deduced from the extrapolation of the cathodic and anodic branches of the Tafel plots. However, the corresponding values are deduced from the extrapolation of the cathodic branch of the Tafel plots to the corrosion potential for MECN and NiC-MCP 8 h because that the anodic polarization curves, which represent oxidation of nickel, do not exhibit a linear behavior [43,44]. The polarization potentials move to positive values and the corrosion current densities decrease 3 and 8 times after hydrothermal carburization for 3 h and 6 h, respectively, indicating that the carbon atoms diffusing into the Ni layer protect the plated Ni metal layer and Si skeleton effectively from KOH. However, excessive carbon diffusion into the Ni layer expands the metal layer as shown in Fig. 1h (NiC-MCP 8 h) consequently decreasing the stability as shown by the low polarization potential and large corrosion current density. After post-annealing, since nanographene is formed on the Ni particles, better stability is observed from MECN (for example, NG-MCP 3 h).

The surface electrochemical properties of the metal electrode can also be investigated by semiconductor electrochemistry [45]. A
Schottky barrier is present at the metal electrode/electrolyte interface with a potential drop and the differential space charge capacitance \((C_{SC})\) can be fitted to the Mott–Schottky equation [45]:

\[
C_{SC}^2 = \frac{2}{e_0 e g A} \left[- (E - E_F) - \frac{k_B T}{e} \right],
\]

(2)

where \(e_0 (e)\) is the vacuum (relative) dielectric constant, \(e\) is the electron charge, \(N_A\) is the volumetric dropping concentration, \(k_B\) is Boltzmann’s constant, \(T\) is the absolute temperature, \(E\) is the applied potential, \(E_F\) is the flat band potential, and the other coefficients have the usual meaning. The space charge capacitance \(C_{SC}\) can be obtained by alternating the voltage in impedance techniques using the following equation [41]

\[
C_{SC} = \frac{1}{2 \pi f \text{Im}(Z)/A}
\]

(3)

where \(A\) is the apparent electrode area, \(\text{Im}(Z)\) is the imaginary part of the impedance data, and \(f\) the frequency (1000 Hz in our case). For the different samples in KOH, the modulus impedances \(|Z|\) and phase degrees versus operating potentials and corresponding differential capacitances are shown in Fig. 5a–c and the related Mott–Schottky plots are presented in Fig. 5d. The flat-band potential is obtained at the crosspoint between the lines of the Mott–Schottky plots and x-axis. The negative slope in the Mott–Schottky plots implies that the passive film on Ni in KOH is p-type and the surface defect concentration \(N_d\) can be estimated based on the slope of the Mott–Schottky plots (assuming \(e = 12\) [41]). The data are also listed in Table 1. The resistance is small, between 3–5 \(\Omega\) cm\(^2\), at high frequencies and introduction of C to the Ni layer enhances the performance of 3D electrode and decreases the solution interface resistance (Fig. 5a). The Ni-C alloy formed on the Ni layer improves the differential capacitance of the 3D electrode (Fig. 5c) and the appropriate amount of carbon (for example, NiC-MCP 3 h) leads to better performance. As shown in Table 1, a larger surface defect concentration \(N_d\) is observed in this case. In this case after the active material Co(OH)\(_2\) deposited on the nano-graphene coated MECN, the the 3D electrodes show a stable capacitance of 3.522 F cm\(^{-2}\) (or 880.5 F g\(^{-1}\)) and excellent electrochemical stability (99%) up to 5000 cycles [37]. Comparing to the flat-band potential of MECN, the values change to the negative potential (about 0.13 V vs. SCE) as carbon diffuses into Ni as shown by NiC-MCP 3 h and 6 h. It corresponds to the accumulation condition in which the majority carriers (here holes) accumulate near the electrode/electrolyte interface [46]. A process involving the opposite sign is necessary in the electrolyte by displacement of anions and cations to compensate charging. However, an excessive amount of carbon over-expands the nickel layer and adversely affects the performance of the localized surface states of the 3D electrode as shown by NiC-MCP 8 h. After post-annealing, the values shift to the positive potential (about 0.3 V vs. SCE) indicating that the surface states of nanographene can localize the minority carrier (electrons) near the electrode/electrolyte interface to form the depletion layer on the electrode. The larger flat-band potential for NG-MCP enables wider application of the 3D electrode in photoelectrolysis and photoelectrochemical devices [47].

4. Conclusion

Nano-graphene is formed on a macroporous electrical conductive network by hydrothermal carbizution and annealing and the electrochemical properties are evaluated by cyclic voltammetry, Tafel plots, and electrochemical impedance spectroscopy. The unique architecture delivers high performance including large Ni content, fast ion transfer process, and small solution interfacial resistance. Because of the different surface properties, the nanographene coated MECN electrode shows p-type semiconducting characteristics, large surface defect concentrations, and positive flat-band potential in alkaline media. The results suggest that the nano-graphene coated MECN electrodes are promising in miniaturized 3D energy storage and photoelectrochemical devices.

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