Fast and reversible surface redox reaction of graphene–MnO$_2$ composites as supercapacitor electrodes

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**ABSTRACT**

We present a quick and easy method to synthesize graphene–MnO$_2$ composites through the self-limiting deposition of nanoscale MnO$_2$ on the surface of graphene under microwave irradiation. These nanostructured graphene–MnO$_2$ hybrid materials are used for investigation of electrochemical behaviors. Graphene–MnO$_2$ composite (78 wt.% MnO$_2$) displays the specific capacitance as high as 310 F g$^{-1}$ at 2 mV s$^{-1}$ (even 228 F g$^{-1}$ at 500 mV s$^{-1}$), which is almost three times higher than that of pure graphene (104 F g$^{-1}$) and birnessite-type MnO$_2$ (103 F g$^{-1}$). Interestingly, the capacitance retention ratio is highly kept over a wide range of scan rates (88% at 100 mV s$^{-1}$ and 74% at 500 mV s$^{-1}$). The improved high-rate electrochemical performance may be attributed to the increased electrode conductivity in the presence of graphene network, the increased effective interfacial area between MnO$_2$ and the electrolyte, as well as the contact area between MnO$_2$ and graphene.

1. Introduction

Supercapacitors, as charge-storage devices exhibiting high-power density, excellent reversibility and cycleability, have attracted tremendous attention due to the growing demand for power systems delivering significant energy in the high-power [1-3]. Most research in this area has been focused on the development of different electrode materials such as various forms of carbon, conducting polymers and transition metal oxides [1,4,5]. Amongst all these materials, manganese oxide has been conceived as a promising supercapacitive material because of its low cost, high electrochemical activity and more friendly environmental nature [6-8]. It is well known that the pseudo-capacitive reaction of MnO$_2$ is a surface reaction, only the surface or a very thin surface layer of the oxide can participate in this pseudo-capacitive reaction [9]. Therefore, ultrathin MnO$_2$ deposits (tens to hundreds of nanometers thick) often deliver very high specific capacitances ranging from 700 to 1380 F g$^{-1}$ [10]. When prepared as micrometer-thick deposits or in composite electrode forms containing carbon and binders, however, MnO$_2$ usually delivers a specific capacitance of only 150–250 F g$^{-1}$ due to the poor electrical conductivity of MnO$_2$ and low accessible surface areas [11]. Thus, a hybrid electrode architecture which incorporates nanoscopic MnO$_2$ film on high-surface-area conductive support (e.g., carbon nanofoams, templated mesoporous carbon, carbon nanotubes (CNTs)) is thought as ideal to optimize both the electrochemical performance and mass-loading of the ultrathin MnO$_2$ [12-15]. Previous approaches to the synthesis of MnO$_2$/carbon composite include various methods as physical mixing [12], thermal decomposition [16], ball milling [17], electrodeposition [18], sonochemical synthesis [19,20], sol–gel [21] and redox reaction [12-15]. Among all these methods, the reduction of aqueous...
permanganate by surface carbon to insoluble manganese oxide, depositing simultaneously as a thin film on the carbon surface, is most attractive due to the inherently self-limiting character of this reaction. However, the overall specific capacitance of MnO2/carbon composites is limited to 250 F g⁻¹ due to the relatively low weight loading of MnO2 on carbon surface (usually less than 64 wt.%) [11,15], at the same time, the capacitance retention ratio over a wide range of scan rates is rather poor (<40% at 100 mV s⁻¹ for MnO2/CNTs) [22–24].

Recently, graphene materials are conceived as extremely promising electrochemical double-layer capacitors (EDLCs) in consideration of its excellent electrochemical performance (135 F g⁻¹) over a wide range of voltage scan rates [25]. The individual sheet does not depend on the distribution of pores in a solid to give its large surface area, resulting in a relatively easy access to the surfaces of graphene materials by the electrolyte while preserving the overall high electrical conductivity for such a network. Obviously, the capacitance may be remarkably improved while maintaining the favorable high-rate electrochemical performance inherent to the special two-dimensional (2D) structure of graphene, if the surfaces of graphene can provide not only the highly reversible pseudocapacitance but also the electrochemical double-layer capacitance [26,27].

In this paper, we reported a rapid and facile method to prepare graphene–MnO₂ composites as novel electrode materials by microwave irradiation. The schematic illustration of the structure of this hybrid material is shown in Fig. 1. For this composite, graphene nanosheets serve mainly as a highly conductive support, which can also provide a large surface for the deposition of nanoscale MnO₂ particles (about 5–10 nm). The excellent interfacial contact and increased contact area between MnO₂ and graphene can significantly promote the electrical conductivity of the electrode due to the high electrical conductivity of graphene. Besides, the easy surface accessibility of this composite by the electrolyte, and the improved electrochemical utilization of MnO₂, resulted from the small particle size and high surface area of the oxides, could provide both the high reversible pseudocapacity and excellent capacitive retention ratio at high charge–discharge rate. Our experimental results show that the composite exhibits overall specific capacitance of 310 F g⁻¹ at 2 mV s⁻¹ and even 228 F g⁻¹ at 500 mV s⁻¹ in aqueous electrolyte, to the best of our knowledge, which are the highest values based on the composites for MnO₂/carbon composites. Furthermore, the composite exhibits very high capacitance retention ratio at high charge–discharge rates (88% at 100 mV s⁻¹ and 74% at 500 mV s⁻¹).

2. Experimental

2.1. Synthesis of graphene materials

Graphite oxide (GO) was synthesized from natural graphite (Qingdao Graphite Company) by a modified Hummers method [28]. As-synthesized GO was suspended in water to give a brown dispersion, which was subjected to dialysis to completely remove residual salts and acids. As purified GO suspensions were then dispersed in water to create a 0.05 wt.% dispersion. Exfoliation of GO was achieved by ultrasonication of the dispersion using an ultrasonic bath (KQ-600KDE, 600 W). In a typical procedure for chemical conversion of GO to graphene, the resulting homogeneous dispersion (100 mL) was mixed with 100 mL of water, 2 mL of hydrazine solution (20 wt.% in water, BASF) in a 250 mL round-bottom flask and the pH of the suspension was adjusted to 10 using sodium hydroxide solution (Beichen Chemical Company), then refluxed at 100°C for 24 h. Finally, the solid was filtered, and washed several times with distilled water and alcohol, dried at 100°C for 12 h in a vacuum oven.

2.2. Synthesis of graphene–MnO₂ composites

Graphene–MnO₂ composites were prepared by redox reaction between graphene and potassium permanganate under microwave irradiation. In the first step, 100 mL of graphene water suspension (1.65 mg mL⁻¹) was subjected to ultrasonic vibration for 1 h. Then KMnO₄ powder (0.0749 or 0.9482 g) was added into above graphene suspension and stirred for 10 min. Subsequently, the resulting suspension was heated using a household microwave oven (Haier, 2450 MHz, 700 W) for 5 min, and then cooled to room temperature naturally. Finally, the black deposit was filtered, washed several times with distilled water and alcohol, and dried at 100°C for 12 h in a vacuum oven. The composition of the composites was adjusted by changing the relative ratio of KMnO₄ to graphene in the starting mixture. The resulting mass percentages of MnO₂ in the composites were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES,
ICPS-7500), and samples are denoted as graphene–20%MnO₂ and graphene–78%MnO₂, meaning that the mass percentages of MnO₂ in the composites are 20 wt.% and 78 wt.% respectively. For comparison, birnessite-type MnO₂ was also synthesized under hydrothermal condition as described elsewhere [29].

2.3. Characterization methods

The crystallographic structures of the materials were determined by a powder XRD system (XRD, TTR-III) equipped with Cu Kα radiation (λ = 0.15406 nm). Raman spectra were recorded with a Raman Station 400F (Perkin–Elmer) using a near infrared laser operating at 785 nm with a CCD detector. X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI 5700 ESCA spectrometer with a monochromated Al Kα radiation (hν = 1486.6 eV). All XPS spectra were corrected using the C 1s line at 284.6 eV. Curve fitting and background subtraction were accomplished using Casa XPS version 2.3.13 software. The N₂ adsorption–desorption isotherms of the samples were measured at 77 K using NOVA 2000 (Quantrachrome, USA) in order to determine the specific surface area (SSA). The SSA was calculated from the Brunauer–Emmett–Teller (BET) plot of the nitrogen adsorption isotherm. The microstructure of the samples was investigated by a scanning electron microscopy (SEM, Camscan Mx2600FE), a transition electron microscopy (TEM, JEOL JEM2010) and an atomic force microscope (AFM, Nanoscope IIIa).

2.4. Preparation of electrodes and electrochemical measurement

The fabrication of working electrodes was carried out as follows. Briefly, the as-prepared materials, carbon black and poly(tetrafluoroethylene) (PTFE) were mixed in a mass ratio of 75:20:5 and dispersed in ethanol. Then the resulting mixture was coated onto the nickel foam substrate (1 cm × 1 cm) with a spatula, which was followed by drying at 100 °C for 12 h in a vacuum oven. The loading mass of each electrode was about 3 mg.

All electrochemical measurements were done in a three-electrode setup: a Ni foam coated with graphene–MnO₂ composites served as the working electrode, a platinum foil electrode and a saturated calomel electrode (SCE) served as counter and reference electrodes respectively. The measurements were carried out in a 1 M Na₂SO₄ aqueous electrolyte at room temperature. Cyclic voltammograms (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) were measured by a CHI 660C electrochemical workstation. CV tests were done between –0.1 and 0.9 V (vs. SCE) at different scan rates of 2, 10, 20, 50, 100, 200 and 500 mV s⁻¹. Galvanostatic charge/discharge curves were measured in the potential range of –0.1 – 0.9 V (vs. SCE) at different current densities of 2, 10, 20 and 50 mA cm⁻², and EIS measurements were also carried out in the frequency range from 100 kHz to 0.1 Hz at open circuit potential with an ac perturbation of 5 mV. The specific capacitance of the electrode can be calculated according to $C = \frac{(\int IdV)}{(\int mV)}$, where $C$ is the specific capacitance (F g⁻¹), $I$ is the response current density (A cm⁻²), $V$ is the potential (V), $m$ is the mass of the electroactive materials in the electrodes (g).

3. Results and discussion

3.1. Microstructure characterizations

The self-limiting deposition of nanoscale MnO₂ on the surface of graphene is used here under microwave irradiation. The reaction is featured by electron transfer from the carbon to the oxidant upon direct contact, and the redox reaction between carbon and K₂MnO₄ in a pH neutral solution is as follows [15]:

$$4\text{MnO}_4^- + 3\text{C} + \text{H}_2\text{O} \rightarrow 4\text{MnO}_2 + \text{CO}_2 + 2\text{HCO}_3^- + 6\text{e}^- \quad (1)$$

In this reaction, the carbon substrate serves as a sacrificial reductant and converts aqueous permanganate (MnO₄⁻) to insoluble MnO₂, which in turn, deposits on the surfaces of graphene (Fig. 1). XRD analysis confirms the monoclinic lamellar structure of birnessite-type MnO₂ (JCPDS 42-1317)
with mixed crystalline and amorphous parts (Fig. 2a). Three broad peaks at 2θ around 12°, 37° and 66° can be indexed to birnessite-type MnO₂ [9]. Broad peaks relate to a poorly crystallized compound originating from the small particle size and approximately amorphous nature of the powder. The peak at 2θ around 43° corresponding to the (1 0 0) crystal plane of graphene cannot be observed after the deposition of MnO₂, indicating that the surfaces of graphene are fully covered by nanoplate MnO₂, resulting in the low degree of graphitization.

The surface information of graphene–MnO₂ composites was collected by XPS, (Fig. 2b). XPS further illustrates the presence of MnO₂ on the surfaces of graphene. The peaks of Mn 2p₃/2 and Mn 2p₁/2 in MnO₂ [30] can be observed in the survey spectrum. The Mn 2p₃/2 peak is centered at 642.1 eV and Mn 2p₁/2 peak at 653.8 eV, with a spin-energy separation of 11.7 eV. These results are in accordance with the previous reported data of Mn 2p₃/2 and Mn 2p₁/2 in MnO₂ [30].

In the Raman spectrum (Fig. 3), the G band (1590 cm⁻¹) represents the in-plane bond-stretching motion of the pairs of C sp² atoms (the E₂g phonons), while the D band (1350 cm⁻¹) corresponds to breathing modes of rings or K-point phonons of A₁g symmetry [31,32]. It is observed that I_D/I_G increases with an increase of the mass-loading of MnO₂ from 20 to 78 wt.%, indicating that more disorder carbon or defects are introduced from the reaction of carbon with MnO₂⁻.

The microstructure images of graphene and graphene–MnO₂ composites are shown in Fig. 4. Graphene from reduction of GO (~1 nm in thickness, ~500 nm in size, Fig. 4a) have wrinkles and folds of edges with thickness of 2–5 nm (inset of Fig. 4b). The BET SSA of graphene is 267 m² g⁻¹, which corresponds to an average flake thickness of approximately 3–4 nm based on the results of the calculations by Jang and Zhamu [33]. And the estimated thickness of graphene is consistent with the observed thickness by TEM (inset of Fig. 4b).

After the redox reaction between carbon and KMnO₄ through microwave irradiation (Fig. 1), it can be seen that the nanoscale MnO₂ particles disperse on the surfaces of graphene (Fig. 4c), and the growth of MnO₂ is prefered near the edges of graphene layer (marked by arrows, Fig. 4c and d) with the size of 5–10 nm (Fig. 4e). Many remained oxygen-containing functionalities (epoxide, hydroxyl, carbonyl and carboxyl groups) on the edges of graphene are vulnerable to oxidation [34–36], and direct electron transfer from sheet defects to MnO₂ results in easy MnO₂ precipitation near the defect sites. Some MnO₂ crystals with the interlayer spacing of 0.7 nm and very thin amorphous MnO₂ coatings are also formed away from the edges of sheets resulted from the reaction of MnO₂⁻ with less active carbon (Fig. 4f).

3.2. Electrochemical behavior

Based on the above considerations, one would expect graphene–MnO₂ with anticipated good electronic conductivity, low diffusion resistance to protons/cations, easy electrolyte penetration, and high electroactive areas to be a promising candidate for the construction of high performance supercapacitors. Up to now, the mechanism proposed for charge-storage of MnO₂-based electrodes in mild electrolytes is ascribed to the rapid intercalation of alkali metal cations such as Na⁺ in the electrode during reduction and deintercalation upon oxidation [37,38].

\[
\text{MnO}_2 + C^+ + e^- \rightleftharpoons \text{MnOOC} \quad (2)
\]

where C⁺ = Na⁺, K⁺, and Li⁺. It should be noticed that the proposed mechanism involved a redox reaction between the III and IV oxidation states of Mn. The CV curves of graphene–MnO₂ composites at a scan rate of 10 mV s⁻¹ in 1 M Na₂SO₄ aqueous solution are shown in Fig. 5a. CV curves of graphene–MnO₂ composites are fairly rectangular shape without obvious redox peaks, indicating that the composites have ideal capacitive behavior. In the case of graphene–78%MnO₂, CV profiles still retain a relatively rectangular shape without obvious distortion with the increasing potential scan rates (Fig. 5b and c). Usually CV curve of MnO₂–carbon composite exhibited a big distortion at a very high scan rate of 500 mV s⁻¹ in previous reports [8,16,22], however, it still retains a relatively rectangular shape in our work, demonstrating excellent high-rate performance. Therefore, the excellent electrochemical performances of graphene–MnO₂ composites may be attributed to their unique microstructures as illustrated in Fig. 1: (1) MnO₂ particles coating on the surfaces of graphene can pile up to form the pores for ion-buffering.
reservoirs to improve the diffusion rate of Na⁺ within the bulk of the prepared materials; (2) nanoscale size of MnO₂ particles (5–10 nm) can greatly reduce the diffusion length over which Na⁺ must transfer during the charge/discharge process, improving the electrochemical utilization of MnO₂, and (3) graphene in the composites act as not only the supports for the deposition of MnO₂ particles but also the electronic conductive channels, and the excellent interfacial contact between MnO₂ and graphene is of great benefit to fast transportation of electron throughout the whole electrode matrix.

The galvanostatic charge/discharge curves of graphene–78%MnO₂ are also shown in Fig. 5d. It can be seen that all the curves are highly linear and symmetrical at various current densities from 10 to 50 mA cm⁻². This implies that the electrode has excellent electrochemical reversibility and charge–discharge properties. Moreover, the iR drops on all curves are similar and not obvious, even at 50 mA cm⁻², indicating little overall resistance and excellent capacitive properties of this hybrid material.

Specific capacitance of graphene and graphene–MnO₂ composites at various scan rates (2–500 mV s⁻¹) is shown in Fig. 6a. It can be clearly observed that graphene–78%MnO₂ exhibits the maximum specific capacitance of 310 F g⁻¹ at 2 mV s⁻¹ in 1 M Na₂SO₄ aqueous solution (even 228 F g⁻¹ at 500 mV s⁻¹), which is almost three times higher than those of pure graphene (104 F g⁻¹) and birnessite-type MnO₂ (103 F g⁻¹). To the best of knowledge, this value is the highest

Fig. 4 – (a) AFM image of exfoliated GO sheets on mica surfaces with height profiles and (b) SEM image of graphene (the inset shows the TEM image of graphene nanosheet with the thickness of about 2–5 nm). (c and d) Low-magnification SEM and TEM images of graphene–78%MnO₂, showing the preferred growth of MnO₂ near the edges of graphene (marked by arrows). (e and f) High-magnification TEM images of small and big square frames in (d), respectively.
values based on the composites for MnO₂–carbon composites. Hence the introduction of MnO₂ as well-dispersed, nanoscale deposits on the conductive graphene surfaces could effectively promote the electrochemical performance of the graphene due to the large pseudocapacity provided by the MnO₂ nanoparticles. In addition, the specific capacitance per unit of SSA calculated at 2 mV s⁻¹ for graphene and graphene–78%MnO₂ is 39 and 110 μF cm⁻², respectively, suggesting that the contribution of MnO₂ redox reactions to the total capacitance is predominant.

An excellent capacitance retention ratio over a wide range of scan rates is another essential character needed for practical application meeting the demand of high-power in supercapacitors. In Fig. 6b, we compare the capacitance retention ratio of graphene–78%MnO₂ with those of MnO₂ film [23], MnO₂/CNT film [24] and birnessite-type MnO₂ at various scan rates. The capacitance retention ratios at 100 mV s⁻¹ are 12%, 31%, 38% and 33% for MnO₂/CNT composite, MnO₂/CNT, MnO₂ and birnessite-type MnO₂, respectively, and the capacitance degenerates very seriously when the scan rates are higher than 100 mV s⁻¹. However, the capacitance retention ratios are still 88% at 100 mV s⁻¹ and even 74% at 500 mV s⁻¹ for graphene–78%MnO₂. This indicates that the increased effective interfacial area between MnO₂ and the electrolyte, as well as the increased contact area between MnO₂ and graphene, resulted from the fair dispersion of nanoscale MnO₂ on conductive graphene, can promote both the electrochemical utilization of MnO₂ and the electrical conductivity of the electrode, the essential characters needed for pseudo-capacitors with high-power density.

The cycle stability of supercapacitors is a crucial parameter for their practical applications. Many reported results show excellent cycling stability of EDLCs consisting of porous carbon due to the nonexistence of pseudocapacitance effect [4]. However, the specific capacitance of activated carbon or porous carbon is often less than 220 F g⁻¹ [39], while functionalized porous carbon with high specific capacitance of 150–300 F g⁻¹ exhibits a poor cycling stability [39] due to the presence of oxygenated groups contributing to the capacitor instability [4], resulting in an increased series resistance and deterioration of capacitance. As for pseudo-capacitive materials, the cycle life of both conducting polymers and metal oxides is much shorter than carbon based materials because structure or volume changes during redox reactions leads to the loss of active materials. Incorporation of pseudo-capacitive materials into carbon materials is effective to improve their cycle performance [40–42]. The cycle stability of the graphene–78%MnO₂ composite was evaluated in this study by repeating the CV test between −0.1 and 0.9 V (vs. SCE) at a scan rate of 500 mV s⁻¹.

Fig. 5 – (a) CV curves of graphene and graphene–MnO₂ composites at 10 mV s⁻¹. (b and c) CV curves of graphene–78%MnO₂ composite at different scan rates of 2, 10, 20, 50, 100, 200 and 500 mV s⁻¹. (d) Galvanostatic charge/discharge curves of graphene–78%MnO₂ composite at different current densities of 10, 20 and 50 mA cm⁻² in 1 M Na₂SO₄ solution.
for 15,000 cycles. The capacitance retention ratio as a function of cycle number is presented in Fig. 7. The capacitance only decreases by 4.6% of the initial capacitance after 15,000 cycles (Fig. 7a), demonstrating excellent electrochemical stability of such electrode material. In the case of the graphene–MnO$_2$ composites, well-dispersed nanoscale MnO$_2$ particles (5–10 nm) on the graphene surfaces can greatly reduce the diffusion length of Na$^+$ during the charge/discharge process, improving the electrochemical utilization of MnO$_2$. In addition, graphene in the composites can provide the electronic conductive channels due to the excellent conductivity of graphene. Furthermore, graphene in hybrid material could provide not only double-layer capacitance to the overall energy storage but also efficient electron transfer channels to improve the electrochemical performances.

The electrochemical impedance spectroscopy (EIS) analysis has been recognized as one of the principal methods examining the fundamental behavior of electrode materials for supercapacitors [1,43]. For further understanding, impedance of the graphene–78%MnO$_2$ composite after the 1st and 15,000th cycles were measured in the frequency range of 100 kHz–0.1 Hz at open circuit potential with an ac perturbation of 5 mV (Fig. 7b). The impedance spectra are almost similar in form with an arc at a higher frequency region and a spike at a lower frequency region, further demonstrating the long-term electrochemical stability of this hybrid material. The measured impedance spectra were analyzed using the complex nonlinear least-squares (CNLS) fitting method [1] on the basis of the equivalent circuit, which is given in the inset of Fig. 7b. At very high frequencies, the intercept at real part ($Z'$) is a combinational resistance of ionic
We present a quick and facile method to synthesize grapheme–MnO2 hybrid for energy storage and conversion applications. For microelectronics, photovoltaic, chemical sensors and the way for successfully employing graphene-based composites. The slope of the 45° portion of the curve is called the Warburg resistance (Zw). This is a result of the frequency dependence of ion diffusion/transport in the electrolyte to the electrode surface. The Warburg impedance is determined from the experimental impedance spectra. A major difference is the semicircle in the high-frequency range, which corresponds to the charge-transfer resistance (Rct) caused by the Faradaic reactions and the double-layer capacitance (Cdl) on the grain surface. The slope of the 45° portion of the curve is determined from the calculated charge-transfer resistance for the electrode resistance is increased from 0.1195 to 0.1301 Ω, which is probably due to the loss of adhesion of some active material with the current collector or the dissolution of some MnO2 during the charge/discharge cycling. Moreover, the increased Warburg resistance after 15,000 cycles is attributed to the increased diffusion and migration pathways of electrolyte ions during the charge/discharge processes.

4. Conclusions

We present a quick and facile method to synthesize graphene–MnO2 composites through the self-limiting deposition of nanoscale MnO2 on the surface of graphene under microwave irradiation. The special structure endows the composite with high-rate transportation of both electrolyte ions and electrons (especially at high rates) throughout the electrode matrix and superior electrochemical utilization of MnO2, resulting in the excellent electrochemical performance. The specific capacitance of graphene–78%MnO2 hybrid is 310 F g⁻¹ at 2 mV s⁻¹, and this capacitance is highly kept over a wide range of scan rates (the capacitance retention ratio is 88% and 74% at 100 and 500 mV s⁻¹). After 15,000 cycles, the capacitance of this electrode only decreases by 4.6% of initial capacitance indicating excellent electrochemical stability. These encouraging results illustrate the exciting potential for high performance, electrical energy storage devices based on this nanostructured graphene–MnO2 hybrid prepared by the fast, cost-efficient, and environment-friendly method. Furthermore, this hybrid material strategy opens up possibilities to combine graphene with other redox pseudo-capacitive materials like polyaniline, polythiophenes, NiO, Co3O4 and RuO2 to enhance the energy density of supercapacitors. We believe that the facile synthesis approach presented here may pave the way for successfully employing graphene-based composites for microelectronics, photovoltaic, chemical sensors and energy storage and conversion applications.

Table 1 – The calculated values of R0, C0, Rct, Zw and Cdl through CNLS fitting of the experimental impedance spectra based upon the proposed equivalent circuit in Fig. 7.

<table>
<thead>
<tr>
<th></th>
<th>R0 (Ω)</th>
<th>C0 (F)</th>
<th>Rct (Ω)</th>
<th>Zw</th>
<th>Cdl (F)</th>
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<tr>
<td>After 1st cycle</td>
<td>0.6680</td>
<td>0.3053</td>
<td>0.1195</td>
<td>0.5735</td>
<td>0.4547</td>
</tr>
<tr>
<td>After 15,000th cycle</td>
<td>0.6612</td>
<td>0.4836</td>
<td>0.1301</td>
<td>0.8004</td>
<td>0.4092</td>
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