Preparation of Foam-like Network Structure of Polypyrrole/Graphene Composite Particles Based on Cellulose Nanofibrils as Electrode Material

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ABSTRACT: Unusual polypyrrole/graphene/cellulose nanofibril (PPy/GR/CNF) composite particles were fabricated by introducing an in situ oxidative polymerization approach. Structural characterization of the composite particles showed foam-like network morphology with a large surface area of 621 m²/g. The PPy/GR/CNF sample exhibited remarkable capacitance behavior in 1 M Na₂SO₄. It showed a high specific capacitance of 264.3 F/g at 0.25 A/g, which represents a 51.7% increase compared to that of PPy/GR and a high capacitance of 155.5 F/g even at a high current density of 5 A/g. Meanwhile, it possessed high rate capability and good cycling performance (85.7% capacitance retention even after 1000 cycles). These excellent electrochemical performances were attributed to the structure of PPy/GR/CNF that can provide large surface areas and shorten electron diffusion pathways. More importantly, the CNF stabilized the structure of PPy and prevented chain breakdown during the charge/discharge process, which improved the cycling performance. Hence, this PPy/GR/CNF composite shows great potential for the fabrication of high-capacitance and low-cost supercapacitor electrode materials with good cycling performance.

INTRODUCTION

With the development of science and technology, portable electronic devices and wearable electronic products have emerged and have been developed rapidly. At the same time, flexible energy storage devices also have received extensive attention. Supercapacitors (SCs) are a new type of energy storage devices that have been developed in recent decades. They have the characteristics of high power density, long cycle life, and good low-temperature performance. They are considered as a bridge connecting the traditional dielectric capacitor and the lithium-ion battery. The most important part of the supercapacitors is the electrode. Carbon materials are usually used as the basis materials for the electrode materials of supercapacitors. However, carbon materials generally have the disadvantage of weak conductivity. In response to this shortcoming, graphene (GR) has been developed rapidly. Because of its unique sp² hybridization structure, GR has the characteristics of ultrahigh conductivity, large specific surface area, good thermal conductivity, and good stability. Therefore, it can be used as the electrode material by itself, and it has also been widely used as the electrode material for supercapacitors.

However, because of its characteristics, GR is prone to exhibit accumulation behavior, which makes it difficult to fully reflect its electrical conductivity and specific surface area. Moreover, carbon materials exhibit only double-layer electrochemical behavior, which limits the storage capacity of the electrode materials. Therefore, we added polypyrrole (PPy) to improve the pseudocapacitance of the composite electrode materials. PPy can exhibit extremely high pseudocapacitance through redox reactions between the electrolyte and N-containing species, which act as electron donors. PPy has outstanding characteristics, such as straightforward synthesis, high electrical conductivity, large pseudocapacitance, and cost-effectiveness. For these reasons, PPy is one of the most studied conducting polymers.

Recently, composites based on conducting polymers and high-power density materials, such as metallic compounds, CNTs, GR oxide, inorganic oxides, and GR, have been studied as a supercapacitor electrode. One outstanding example of these composite materials is PPy/GR, which can be fabricated by a simple method and shows the properties of GR, such as a two-dimensional carbon nanostructure, excellent electronic transport properties, good mechanical stiffness, and high thermal and electronic conductivity. Biswas and Drzal prepared a PPy/GR composite using a simple and...
effective ultrasonication comixing method and reported its specific capacitance (SC) to be 165 F/g at a current density of 1 A/g. Although several efforts have since been made, unfortunately, the electrochemical performance of PPy has yet to be improved upon. There are two reasons for this: (1) the composite materials have inaccessible surfaces, which considerably reduce the actual capability of the capacitance and (2) CPs commonly undergo structural breakdown because of the considerable volume change induced by the repeated intercalation and depletion of ions. The results show that the cyclic stability of composites is poor.

To solve this problem, we added nanocellulose to improve the wettability of the composites and to increase the contact between the composites and the electrolyte. Cellulose nanofibrils (CNFs), which are derived from natural cellulose fibrils by controlled acid hydrolysis, have drawn considerable interest owing to their various attractive properties, such as the high density of active surface groups, high aspect ratio, large specific surface area, good water dispersibility, attractive mechanical properties, and prospect for environmental sustainability. Furthermore, CNFs have a multichannel mesoporous structure, which is ideal for the absorption and transport of water and essential ions through the outer and inner surfaces of fibers, acting as an electrolyte reservoir. These features make the CNF composite of PPy particularly interesting for enhancing the performance of supercapacitors.

In this work, the electrode material for the foam-like network structure containing PPy and GR was successfully synthesized via a CNF-assisted, facile, low-energy, in situ polymerization method. The advantages of using CNFs for enhancing the electrochemical properties of PPy/GR are as follows: (1) the natural structure of CNFs allowed them to form an expanded network structure and (2) they act like a template to adsorb Py monomers onto the structure of CNFs during the subsequent polymerization step. It is worth noting that we explored the effects of CNF concentration on the electrochemical properties of the composite particles; they have not been studied by any research group as well. We prepared five composites with different weights of CNFs in order to obtain the best performance PPy/GR/CNF composite material.

**EXPERIMENTAL SECTION**

**Materials.** Bleached wood pulp was provided by Shandong (Ri Zhao, China). GR was purchased from Tanfeng Tench Inc. Other common reagents were purchased from Beijing Chemical Plant and are of analytical grade. The combination of pretreatment and homogenization processes improved the dispersion of CNFs in deionized water.

**Preparation of PPy/GR/CNF Composite Particles.** PPy/GR/CNF composite particles were prepared by an in situ chemical oxidative polymerization method. In a typical procedure, 50 mg of GR was first dispersed in deionized water containing CNFs (1 mg/mL). The whole solution was ultrasonicated for 4 h. A 1 mL portion of pyrrole was slowly added to this dispersion with stirring, followed by a slow addition of 50 mL of FeCl$_3$ solution. The resultant mixture was stirred vigorously for 30 min to form the PPy nanocomposite in the solution. The whole solution was then stirred for 24 h at 0–4 °C. After polymerization, the composite particles were filtered and thoroughly washed with ethanol and deionized water in sequence several times to ensure the removal of residual FeCl$_3$ from the composites. The mixture was finally dried at 65 °C overnight to obtain the PPy/GR/CNF composite particles. Composite particles containing 200, 100, 50, 25, and 0 mg of CNFs were denoted as PPy/GR/CNF-200, PPy/GR/CNF-100, PPy/GR/CNF-50, PPy/GR/CNF-25, and PPy/GR, respectively.

**Characterization and Measurement.** The morphology of the as-prepared products was studied using a scanning electron microscope (SEM) and transmission electron microscope (TEM). The electrochemical properties of the composites were measured using a three-electrode system with a Au electrode as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) measurements were performed using a CHI660D electrochemical workstation.
An electron microscope (Hitachi S-4800) operated at 20 kV. The chemical structure of PPy/GR/CNF-50 was ascertained by Fourier transform infrared spectroscopy (FT-IR, VERTEX TOV), Raman spectra (Horiba Scientific LabRAM HR Evolution), and X-ray photoelectron spectroscopic (XPS) measurements with an Escalab250xi (Kratos AXIS SUPRA, 1486.69 eV). Nitrogen gas adsorption and desorption isotherms were obtained with an ASAP 2020 instrument (Micromeritics, USA) at 77 K. Composite particles were degassed at 100 °C for 12 h before the measurements. Their specific surface area was estimated according to the Brunauer–Emmett–Teller (BET) method based on the adsorption isotherms. The electronic conductivity of PPy/GR/CNF-50 was measured by four point probe resistivity meter (Guangzhou 4-probes Test, RTS-9). The sample was processed into 1 × 1 cm2 slices before characterization (<1 mm thickness). Thermogravimetry analysis (TGA) was performed under a nitrogen flow from room temperature to 600 °C at a heating rate of 20 °C/min using a TGA Q50 (TA Instruments).

**Electrochemical Measurements.** Dried activated samples, including PPy/GR/CNF-200, PPy/GR/CNF-100, PPy/GR/CNF-50, PPy/GR/CNF-25, and PPy/GR were ground in an agate mortar. Working electrodes were fabricated by mixing the sample with acetylene black and 60% polytetrafluoroethylene in a mass ratio of 85:10:5. The mixture was dispersed in an aqueous C2H5OH solution to form a homogeneous slurry, which was then coated onto a stainless steel nickel foam (1.0 cm × 1.0 cm) and dried under vacuum at 60 °C for 24 h. The mass loaded onto the electrode was about 5 mg. The electrochemical performances of the materials were evaluated with a CHI 760D electrochemical station (CH Instruments, USA) by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) measurements, and electrochemical impedance spectroscopy (EIS) on a three-electrode system with a platinum electrode and a saturated calomel reference electrode. Na2SO4 (1 M) solution was used as the electrolyte and was purged with nitrogen for 15 min prior to the measurements. The cell capacitance was determined from the CV curve using the equation

\[ C_m = \frac{I \times \Delta t}{\Delta V \times ma} \]

where \( C_m \) is the specific capacitance per unit mass of composite particles in the electrode (F/g), \( I \) is the discharge current (A), \( \Delta t \) is the time elapsed for the discharge from −0.5 to 0.5 (V), \( \Delta V \) is the voltage difference within that time (s), \( a \) is the mass of the active substance (composite particles) on the electrode (%), and \( m \) is the mass of the electrode (g).

**RESULTS AND DISCUSSION**

To better understand the preparation process of PPy/GR/CNF, the experimental process is schematically shown in Figure 1. GR was first dispersed in deionized water with CNFs by ultrasonication. Then, pyrrole was added to the mixture followed by slow addition of FeCl3 under stirring. At the same time, the FeCl3 solution can enable Py to polymerize into PPy, which is uniformly coated on the surface of GR and CNFs. The solution was filtered, washed, and dried to get composite particles. The presence of CNFs in composites led to the formation of an extended foam-like network structure, which facilitated the accessibility of the electrolyte. Clearly, the LED lamp was faintly lit when the PPy/GR/CNF-50 composite was part of the wire (Figure 1). The high electronic conductivity of the obtained PPy/GR/CNF-50 was 4.99 S/cm.

Figure 2 shows the SEM images of PPy, PPy/GR, and PPy/GR/CNF-50. The pure PPy shows polymer domains with a diameter of 200 nm (Figure 2a,d). A thick coating of PPy on GR was observed for PPy/GR (Figure 2b,e), whereas when CNFs were added under the same conditions, the samples showed a different morphology from that of previous structures (Figure 2c,f). The decoration of PPy/GR with CNFs created a foam-like network structure, which could increase the surface area and allow more access to the electrolyte. The detailed microstructures of PPy/GR/CNF-50 were investigated; PPy distributed on the surface of the CNF.
and changed the morphology of PPy from particles to that of nanofibrils. During polymerization, CNFs acted like a template to give PPy their nanofibril morphology. This might be explained by the chemical interactions between the NH groups of pyrrole and the OH groups on the surface of the CNF. With the increase of CNF content in the composite particles, the structure of nanofibrils (PPy distributed on the surface of the CNF) was formed (Figure 2g,h). However, a sheet-like morphology was found when the CNF was present in excess in the composite particles, as shown in Figure 2i. This morphology may be attributed to the presence of an even larger amount of OH groups from CNFs, which promoted the formation of PPy on its surface.

It is well known that the Py monomer possessed a typical conjugated structure, which may facetly link with the surfaces of GR and CNFs via π–π interaction or H-bonding. This would be further demonstrated by the FT-IR spectra, as shown in Figure 3a. The FT-IR spectrum of CNFs appeared as a broad band at 3409 cm$^{-1}$, which is the characteristic of the cellulose O–H group. The band at 2916 cm$^{-1}$ is attributed to the asymmetric stretching vibration of C–H. The spectral features of pure PPy were well known in the literature, and the spectrum shows broad characteristic peaks derived from various stretching modes at 3400 cm$^{-1}$ (N–H), 1560 cm$^{-1}$ (C=C), and 1531 cm$^{-1}$ (C–C). In the case of PPy/GR, it possessed all the characteristic absorption peaks of PPy, but with weaker peak intensities for the characteristic peaks of PPy. Therefore, it is evident that PPy was indeed loaded onto the surface of GR via interactions such as hydrogen bonding and π–π stacking between them. When CNFs were added under the same conditions, the characteristic absorption of CNFs in PPy/GR/CNF-50 appeared as weak shifting of the characteristic bands, indicating the presence of PPy on CNFs. The bands at 1531 cm$^{-1}$ (1544 cm$^{-1}$ for PPy/GR/CNF-50) are assigned to the C–C stretching vibrations in the pyrrole ring. The observed shift of this band might be attributed to the
bonding between the −NH group in the pyrrole ring and the −OH group of the CNF, as suggested by Johnston et al.32 However, there was the CNF absorption peak in PPy/GR/CNF-50, possibly because the CNF was distributed in the material and covered by a layer of PPy on the surface, covering its characteristic peak. But compared with PPy/GR/CNF-50, PPy/GR/CNF-200 has a strong absorption peak of CNF in 2916 cm⁻¹, which may be caused by the free CNF in the material. Thus, FT-IR results confirmed the possible interaction between PPy, GR, and CNFs, which was responsible for the successful formation of PPy/GR/CNF.

The Raman spectrum (Figure 3b) shows two peaks around 1340 cm⁻¹ (D-band) and 1550 cm⁻¹ (G-band). The G-band peak at 1550 cm⁻¹ that stemmed from E₂g phonon vibrations of sp²-bonded carbon atoms is a characteristic feature of graphite layers, and the D-band peak at 1340 cm⁻¹ attributed to the breathing mode of k-point phonons with A₁g symmetry is related to the defective graphic structure and disordered carbon (sp³ rich phase).33 The intensity ratio (I_D/I_G) indicated that the material has a high degree of conjugation. It further shows that the composite material has good electrical conductivity (Figure 4).34

The chemical composition of PPy/GR and PPy/GR/CNF-50 was determined by XPS. XPS data suggest that PPy/GR contains 75.54 mol % carbon, 11.98 mol % oxygen, and a small amount of 12.48 mol % nitrogen. PPy/GR/CNF-50 contains 76.55 mol % carbon, 14.56 mol % oxygen, and 8.89 mol % nitrogen. The addition of CNFs increases the overall oxygen content of the material, which was caused by a large number of oxygen-containing functional groups on the surface of CNFs. The XPS C 1s spectrum of PPy/GR shows a single peak composed of sp²-bonded carbon (284.8 eV), and its small tail contains sp³-bonded carbon (285.5 eV). The XPS C 1s spectrum of PPy/GR/CNF-50 shows a single peak composed of sp²-bonded carbon (284.8 eV) and sp³-bonded carbon (285.4 eV), and its small tail contains C=O (287.8 eV) and C=O (286.8 eV). The XPS O 1s spectrum of PPy/GR/CNF-50 shows a single peak composed of C=O (529.2 eV), and its small tail contains C=O (530.9 eV). The XPS N 1s spectrum of PPy/GR/CNF-50 shows a single peak composed of N—H (399.7 eV), and its small tail contains N— (400.8 eV). These indicate that CNFs and PPy have been successfully added to the materials, and the materials had a rich conjugate structure, which provides excellent conductivity to the material.35 These results are also consistent with those obtained by IR analysis and Raman analysis. In addition, oxygen-containing groups on the surface of CNFs enhance the wettability of electrodes and electrolytes, while the electron-rich nitrogen also enhances the conductivity of carbon materials. Furthermore, these surface heteroatom-doped functional groups could be used as additional active sites of pseudo-capacitance to improve the electrochemical properties of materials.

The N₂ adsorption−desorption isotherms, as shown in Figure 5, were used to determine the surface area and the pore-size distribution of PPy/GR/CNF-50 as compared to PPy/GR. The nitrogen adsorption isotherms of PPy/GR/CNF-50 and PPy/GR (Figure 5a) show type II and type IV isotherm characteristics (characterized by a hysteresis loop). The BET surface area of PPy/GR was calculated to be 135 m²/g, as described in the literature.37 The reason for such a low surface area of PPy/GR was the compact coating of PPy on the GR, as demonstrated by SEM images. However, this value increased to 621 m²/g after CNF incorporation into the PPy/GR system. This enhanced surface area could be attributed to the foam-like network structure, which expanded the interspacing and thus increased the surface area. As shown in Figure 5b, a hierarchical broad pore size distribution with a combination of mesoporous (2−5 nm) and macroporous (>50 nm) structures was obtained from the N₂ adsorption−desorption isotherms.

The effect of CNF percentage on the thermal stability of the composite was analyzed by TGA, as shown in Figure 6. Most of the samples exhibited some release of the absorbed moisture at approximately 100 °C. As to CNFs, two stages were identified: (1) the degradation of CNFs involving the formation of various anhydromonosaccharides (including levoglucosenone, levoglucosan, and 1,6-anhydro-b-D-glucopyranose) from 257 to 436 °C and (2) the degradation of CNF−OH bonds from 436 °C to 549 °C.39 Compared with

Figure 5. Nitrogen adsorption−desorption isotherms of PPy/GR/CNF-50 (a) and PPy/GR and pore size distribution profiles of PPy/GR/CNF-50 (b).

Figure 6. TGA curves of CNFs, PPy/GR, PPy/GR/CNF-50, and PPy/GR/CNF-200.
CNFs under the same conditions, it can be seen that PPy/GR shows less mass loss, indicating its better thermal stability. The TGA curves of PPy/GR and PPy/GR/CNF show a similar shape, where the profile of PPy/GR/CNF lies between the profiles of CNF and PPy/GR. Moreover, the similarities in the TGA profile between the CNF and PPy/GR suggest the introduction of CNFs into the PPy/GR system.40 After that, the massive weight loss of PPy/GR/CNF-50 happened at 291 °C which was higher than PPy/GR/CNF-200 (271 °C). In other words, with the increase of CNF content in the PPy/GR system, the PPy/GR/CNF exhibited bad thermal stability. This may be due to the presence of higher amounts of −OH during the in situ polymerization reaction and the intermolecular hydrogen bonding between CNF and PPy.41 The above results illustrate the influence of CNF on the thermal stability of PPy/GR/CNF.

CV is a potentiodynamic electrochemical measurement that can be used to measure the specific capacitance of electrode materials. In order to evaluate the effects of the incorporated CNF on the electrochemical performance, we performed CV experiments, as shown in Figure 7a,b. Figure 7a shows the representative CV scans of all samples performed at a scan rate of 100 mV/s in 1.0 M Na2SO4 aqueous solution, and obvious redox peaks cannot be observed in all samples. This result could be explained by the transport and diffusion of counterions into the structure, which was slow compared to the rate of electron transfer in PPy at high scan rates.42 Nevertheless, PPy/GR/CNF-50 produced larger currents than other samples, indicating that the incorporated CNF enhanced the electrochemical performance of the GR/PPy composites. To further explore the electrochemical properties of PPy/GR/CNF-50, CV measurements were performed at different scan rates from 10 mV/s to 100 mV/s, as shown in Figure 7b. The CV curves exhibited a distorted rectangular shape, which suggests good capacitance behavior. However, the shape of the CV curves gradually transformed from an ideal rectangle to an oval with increasing scan rate. This may be attributable to the inhibition of charge collection by the internal resistance of the electrode, the low conductivity of Na2SO4 aqueous solution, and the diffusion limitations of Na+ in the electrode.43 Figure 7c shows the GCD curves of all the samples at a current density of 1 A/g. The corresponding specific capacitance (SC) values were calculated using eq 1. The SC values of PPy/GR, PPy/GR/CNF-25, PPy/GR/CNF-50, PPy/GR/CNF-100, and PPy/GR/CNF-200 were 83.3, 165.6, 223.8, 119.1, and 97.7 F/g, respectively. These results agreed with the trends revealed by CV measurements. However, it can be found from the results that the overall composite material is lower than the high-performance and breathable PPy-coated air-laid paper (3100 mF·cm−2 at 1 mA·cm−2) studied by Chen et al. and the ultrahigh performance and flexible PPy-coated CNT paper electrode (8604.5 mF·cm−2 at 1 mA·cm−2) studied by Cai et al. It may be caused by the partial agglomeration of GR. The SC of PPy/GR/CNF-50 was higher than that of other samples. The behavior of the capacitance of PPy/GR/CNF-50 was examined at different current densities in the range 0.25–5 A/g, as shown in Figure 7d. The discharge curve indicated the SC values of 264.3, 223.8, 181.8, and 155.5 F/g at 0.25, 1, 2, and 5 A/g, respectively. The steady decrease of SC could be attributed to the diffusion limitations and the decrease of pseudocapacitance with increasing current density.44 However, all the GCD curves exhibited a nearly symmetrical triangular shape and straight discharge slopes, suggesting good electrochemical capacitive behavior with a small IR drop and excellent reversibility of the charge/discharge process.45,46

The EIS technique was employed to explore the ionic/electronic transport pathways in GR/PPy/CNF. Figure 8 shows the EIS curves of all samples, which were used to investigate the redox (charge/discharge) process of electrode
materials and to evaluate their electronic and ionic conductivity. The inset in Figure 8 corresponds to the high-frequency region of Nyquist plots. In the high-frequency region, the diameter of the arc reflected the charge transfer resistance ($R_{ct}$), which is related to the interfacial processes of counterions at the electrode/electrolyte interface. The $R_{ct}$ values of all PPy/GR/CNFs were significantly smaller than that of PPy/GR. PPy/GR/CNF-50 shows the smallest $R_{ct}$ of approximately 1.57 $\Omega$. After the semicircular region, a straight line at an angle of 45$^\circ$ in the low-frequency range is observed, which corresponds to the Warburg diffusion resulting from the frequency dependence of ion diffusion/transport in the electrolyte.$^{47}$ The larger Warburg resistance indicates greater variations in ion diffusion path lengths and increases the obstruction of ion movement.$^{35}$ It can be observed that the slope of the impedance plots increased first and then decreased with increasing CNF content in the composite particles, while that of PPy/GR/CNF-50 was the smallest. The reduced resistance of the composite might be due to the foam-like network structure of PPy/GR/CNF, which facilitated the efficient access of electrolyte ions to the PPy/GR/CNF surface and shortened the ion diffusion path. This agreed with the outcomes of SEM and CV tests.

To further explore the electrochemical properties of PPy/GR/CNF-50, we compared the performances of PPy/GR/CNF-50 and PPy/GR, as shown in Figure 9. The SC values of PPy/GR/CNF-50 and PPy/GR at different current densities were obtained from Figure 9a. The maximum value of 264.3 F/g was obtained at a current density of 0.25 A/g, which represented a 51.7% increase compared with that of PPy/GR. We conclude that the SC value obtained for GR/PPy/CNF-50 was higher than many previously reported values for the composite based on PPy.$^{3,48-51}$ Furthermore, the IR drop of PPy/GR at 5 A/g was 0.34 V and that of PPy/GR/CNF-50 was only 0.15 V (Figure 9b). The lower IR drop depended mainly on the smaller equivalent resistance and was associated with more rapid diffusion and exchange of electrons and counterions in PPy/GR/CNF-50.$^{52}$ These results are consistent with our observations of EIS and can most likely be ascribed to the structure of the materials. As shown in Figure 9c, the cyclic stabilities of PPy/GR/CNF-50 and PPy/GR were investigated by continuous charge/discharge cycle tests at a current density of 5 A/g in the Na$_2$SO$_4$ electrolyte. The capacitance retention of PPy/GR/CNF-50 decreased to 85.7% of its initial value over 1000 cycles, while the capacitance retention fell to 71.5% for PPy/GR. The clearly enhanced cyclic stability of the composite resulted from the electron-conductive pathways of the interpenetrating conducting network of the CNF, which stabilized the structure of PPy and prevented chain breakdown during the charge/discharge process.

Figure 8. EIS curves of PPy/GR and PPy/GR/CNF.

Figure 9. Electrochemical properties of PPy/GR and PPy/GR/CNF-50: SC (a) and IR drop (b) at different current densities; cycling performance from the 1st to the 1000th cycle at a current density of 5 A/g (c).
CONCLUSIONS

A novel foam-like network structure of GR/PPy/CNF had been successfully fabricated using a facile, low-cost, nontoxic, and environmentally friendly in situ polymerization method. The GR reduced the charge transfer resistance and increased the rate of electrochemical reactions in the bulk PPy. Controlled addition of CNFs was carried out to improve the electrochemical properties during the polymerization process. The as-obtained GR/PPy/CNF possessed a unique foam-like network structure with a high surface area. These promising results revealed that natural CNFs were added to produce advanced materials with high capacitance and good cycling performance in supercapacitor. As a result, the charge storage was improved, rendering a high SC at high current densities.

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Notes

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