

Article

Composite Cathodes Based on Lithium-Iron Phosphate and N-Doped Carbon Materials

Irina Stenina ^{1,*}, Danis Safikanov ¹, Polina Minakova ¹, Svetlana Novikova ¹, Tatiana Kulova ² and Andrey Yaroslavl'tsev ¹

¹ Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky Prospekt 31, Moscow 119991, Russia

² Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky Prospekt 31-4, Moscow 119071, Russia

* Correspondence: stenina@igic.ras.ru; Tel.: +7-(495)-7756-585

Abstract: The effect of different nitrogen-doped carbon additives (carbon coating from polyaniline, N-doped carbon nanotubes, and N-doped carbon nanoparticles) on electrochemical performance of nanocomposites based on the olivine-type LiFePO_4 was investigated. Prepared materials were characterized by XRD, SEM, TGA-MS, CHNS-analysis, IR-, Raman, and impedance spectroscopies. Polyaniline deposition on the LiFePO_4 precursor with following annealing lead to the formation of a LiFePO_4/C nanocomposite with a carbon coating doped with nitrogen. Due to nitrogen atoms presence in carbon coating, the LiFePO_4/N -doped carbon nanocomposites showed enhanced conductivity and C-rate capability. The discharge capacities of the synthesized materials in LIBs were close to the theoretical value at 0.1 C and retained high values with increasing current density. At high C-rates, the best results were obtained for a more dispersed LiFePO_4/C composite with carbon coating prepared from polyaniline previously in situ deposited on LiFePO_4 precursor particles. Its discharge capacity reached 96, 84, 73, and 47 mAh g^{-1} at 5, 10, 20, and 60 C-rates, respectively.

Keywords: LiFePO_4 ; carbon coating; nitrogen-doped carbon; CNT; PANI; cathode; lithium ion battery



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1. Introduction

The olivine-type lithium-iron phosphate LiFePO_4 , hereafter LFP, is recognized as a promising cathode material for lithium-ion batteries (LIBs) owing to its safety, good stability, high theoretical capacity (170 mAh g^{-1}), and low cost [1]. The main limitation for the LFP applications as cathode is its low conductivity. At room temperature, electronic conductivity of LFP is about $10^{-9} \text{ S cm}^{-1}$, while lithium diffusion coefficient is $\sim 10^{-14}$ – $10^{-16} \text{ cm}^2 \text{ s}^{-1}$ [2,3]. Low electronic conductivity leads to a fall of charged-discharge capacity at increased C-rates and hinders the LFP use at temperatures below zero [4], and in devices requiring high peak power [5].

There are many approaches for LFP conductivity improvement: the preparation of nanomaterials [1,5–9], a partial substitution of lithium, iron or phosphorus by other elements [6,10–15], and the composite formation [4,8,16–24]. As a result of decrease in the particle size, the diffusion length of Li^+ ions and electrons to grain boundaries, where charge transfer usually occurs much faster than it does in the bulk, also decreases. Most often, a combination of the above approaches is used. Formation of composites with conductive additives improves electron transfer at grain boundaries. Conductive polymers (polypyrrole, polyaniline (PANI) or poly(3,4-ethylenedioxythiophene)) [16,21,25–27], as well as various carbons (carbon black, graphite, carbon nanotubes (CNTs), graphene, etc.) [18,23,28–31] are being used as conductive additives. Carbon coating is considered as one of the most effective ways to improve the LFP conductivity. In the most cases, it is performed by carbon source addition to materials or their precursors, followed by thermal treatment in an inert atmosphere. Availability and low cost of many carbon sources are its

main advantages. Moreover, carbon coating can help to avoid agglomeration of LiFePO_4 particles during the annealing process and contributes to the formation of a finer material. Thus, the main problem is to obtain an optimal carbon coating layer to produce electrode materials with enhanced battery performance.

A number of researchers have noted the unique physical and chemical properties of nitrogen-containing carbon materials (CN_x , $x < 1$), most notably, an improved electronic conductivity compared to undoped ones [32,33]. A combination of carbon coating and N-doping can result in an enhancement of conductivity and facilitate transport of lithium ions and electrons. Polydopamine, polyaniline, and polybenzoxazines with heteroatoms in the main chain are considered to be promising carbon and nitrogen sources for the preparation of composites with N-doped carbon [34–38]. The number of works devoted to the polyaniline use as N and C bi-source is small. Avci et al. used a solid-state reaction and a previously prepared chloride-doped PANI to synthesize $\text{LiFePO}_4/\text{CN}$ composites [35]. The $\text{LiFePO}_4/\text{CN}$ electrode exhibited a reversible capacity of 164 mAh g^{-1} at 0.1 C and an improved rate capability compared to that of LiFePO_4/C prepared using sucrose as a carbon source. Moreover, the in situ polymerization of aniline with the following PANI carbonization can result in a more uniform carbon coating, as is the case with dopamine [39]. Yan et al. used a carbothermal reduction method to synthesize LFP/C composite from $\text{FePO}_4/\text{polyaniline}$ prepared by in situ polymerization-precipitation and sucrose [38]. However, when using this method, it is difficult to control and maintain the temperature to produce a single-phase LFP, and carbon coating is prepared not only from polyaniline. Therefore, the question remains about the optimal method for LFP/ C_{PANI} manufacturing. There are relatively few studies on composites of LFP with nitrogen-doped carbon nanomaterials (N-doped CNTs, N-doped graphene, etc.) [20,40–42]. In forming composites, carbon nanomaterials usually act as bridges between electrode material particles, providing a high charge transfer rate and good electrochemical performance, which is primarily due to their high conductivity. The charge–discharge rate is determined by the rate of charge transfer through LFP particles to grain boundaries and in an intergranular space filled by carbon coating. This depends on a combination of such characteristics as the LFP particle size, its electronic and ionic conductivity, the rate of lithium ion and electron transfer in the carbon coating, and contact between LFP particles and carbon in the composite. Despite an increased interest in conductivity of electrode materials, this is not the only determinant of their electro-chemical properties. Moreover, the use of substantially different techniques and conditions of the composite manufacturing poses problems for comparing effects of various carbon additives on the electrochemical performance of composites. Despite the fact that the positive effect of carbon additives is currently confirmed, a little attention has been paid to their thorough and systematic investigation.

In this study, to determine the most appropriate strategy of nitrogen-doped carbon introduction, the effect of various N-doped carbons (carbon coating, CNTs, and carbon nanoparticles) on the electrochemical performance of prepared composites was studied. Novel composites based on LFP with N-doped carbon were prepared using an in situ sol-gel technique. A simple and low-cost procedure for manufacturing of composites based on LFP and a highly conductive carbon coating containing nitrogen atoms via pyrolysis of polyaniline layer previously deposited on the LFP using was proposed and optimized. The effect of the aniline/LFP molar ratio and the order in which reagents were added during aniline polymerization on the properties of the resulting composites were studied for the first time. As a result, prepared composites exhibited a superior performance as LIB cathodes.

2. Materials and Methods

2.1. Material Manufacturing

N-doped carbon nanotubes (N-CNTs) and N-doped carbon nanoparticles (N-CNPs) were prepared using a CVD (chemical vapor deposition) method by flowing acetonitrile at 750–850 °C over a fixed layer of Co/MgO (MgO) used as catalyst for the synthesis of

N-CNTs (N-CNPs). The prepared carbon nanomaterials were then washed with HCl and deionized water and dried.

Lithium iron phosphate was prepared by a sol-gel technique described elsewhere [15,29] using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98+%, Sigma Aldrich), LiNO_3 (99+%, Sigma Aldrich), and $\text{NH}_4\text{H}_2\text{PO}_4$ (98+%, Sigma Aldrich). The stoichiometric amounts of initial reagents were dissolved in deionized water, which was followed by evaporation at 85 °C under constant stirring. The resulting mixture was heat-treated at 300 °C for 4 h to remove gaseous products. The as-prepared LFP precursor was coated by polyaniline or ground with 5 or 10 wt.% N-CNTs (N-CNPs) and sucrose as a carbon source in an agate mortar. In this work, grinding in an agate mortar was used rather than high energy ball-milling since it was shown that the latter, commonly used for the composite manufacturing, results in partial destruction of carbon nanomaterials and deterioration of electrochemical performance of obtained LFP cathodes [43]. The LFP/C composite, prepared in the same way using sucrose as a carbon source without carbon nanomaterials, was used as a reference sample.

The deposition of a PANI film on the LFP precursor surface was carried out by the in situ oxidative polymerization (Figure 1) using aniline (ANI, Sigma Aldrich, 99%) as a monomer, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Sigma Aldrich, 98+%) as an oxidant, and HCl (Sigma Tech, analytical grade). The ANI/LFP molar ratios were 0.125–1. According to the first method (method I), a mixture of 0.1 M ANI.HCl solution and the LFP precursor was kept under stirring for 15 min at 25 °C. Next, an equal volume of 0.125 M aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was added at ~5 °C and stirred for 45 min. In the second case (method II), the LFP precursor was placed in the deionized water (10 mL of water per 5 mmol of LFP) and ultrasonically treated for 1 min. A specified amount of ANI was added to this suspension and stirred for 30 min. A cold 0.125M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution and HCl (to achieve pH = 1) was then added and stirred for 45 min at ~5 °C. In both methods, prepared materials were filtered, washed with water, dried in air, and ground in an agate mortar. Further, all the LFP-precursors with either PANI or N-doped carbon nanomaterials were calcined at 650 °C in argon atmosphere for 10 h. Hereafter, the LFP composites with N-CNTs and N-CNPs are denoted as LFP/C/5N-CNT, LFP/C/10N-CNT, LFP/C/5N-CNP, and LFP/C/10N-CNP, respectively. The number in the composite name denotes the amount (wt.%) of N-doped carbon used. The LFP/C composites prepared by method I and II using PANI as both nitrogen and carbon sources are denoted as LFP/C_{PANI}-I and LFP/C_{PANI}-II, respectively.

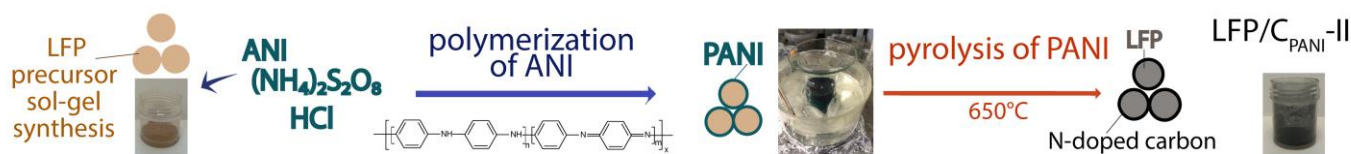


Figure 1. The schema of the LFP/C_{PANI}-II formation.

2.2. Methods

Phase composition of the prepared materials was analyzed by X-ray diffraction (XRD) using a Rigaku D/MAX 2200 diffractometer ($\text{CuK}\alpha$ radiation) and FullProf Suit software. The LFP crystallite size (d) was calculated from the broadening of the XRD peak with Miller indices (311) using the Scherrer formula (1):

$$d = \frac{k\lambda}{\sqrt{B^2 - b^2} \cos \theta}, \quad (1)$$

where λ is the X-ray wavelength, θ is the diffraction angle, k is the Scherrer constant, $k = 0.9$, b is the instrumental broadening determined using a LaB_6 SRM 660a standard, and B is the peak width at half-maximum. The error of the crystallite size determination did not exceed ± 2 nm. IR spectra were registered on a Nicolet iS5 FTIR spectrometer using attenuated total reflection techniques on an attachment with diamond crystal. Raman spectra were registered using a DXRxi Raman Imaging Microscope and a 532 nm laser with power

of 0.2–0.6 mW. The morphology of the samples was analyzed using a scanning electron microscope (SEM) Tescan Amber (Tescan, Czech Republic) equipped with an AZtec system (Oxford Instruments) for energy-dispersive X-ray spectroscopy (EDS) data analysis. SEM images were taken at an accelerating voltage of 2 kV. Transmission electron microscopy (TEM) was performed using a Hitachi HT7700 transmission electron microscope at an accelerating voltage of 100 kV. The low-temperature nitrogen adsorption isotherms were measured using a Sorbtometer-M analyzer at 196 °C. Both carbon and nitrogen contents in the samples were measured using a EuroVector EuroEA3000 elemental analyzer. To provide additional evidence of the N-doped carbon coating formation with PANI pyrolysis, thermogravimetric analysis-mass spectrometry (TGA-MS) was performed on a Netzsch TG 209 analyzer in air in the temperature range of 25–800 °C at a heating rate of 10 °C min^{−1}. Gas phase composition was analyzed on an Aeolos QMS 403C mass spectrometer.

Electrochemical tests were performed in sealed three-electrode cells assembled in a glove box in Ar atmosphere (humidity level < 10 ppm). The LFP-based composite (the working electrode) was deposited on the stainless steel gauze (current collector) as a 5–7 mg cm^{−2} layer. A polypropylene separator was used between the working (the LFP-based composite), auxiliary, and reference (both lithium) electrodes. The surface area of working and auxiliary electrodes was 2.25 and 5 cm², respectively. The electrolyte was 1 M LiPF₆ in a mixture of ethylene carbonate-diethyl carbonate-dimethyl carbonate (volumetric ratio 1:1:1; content of residual water ≤ 20 ppm). Electrochemical cycling in a galvanostatic mode was performed in the potential range of 2.5–4.1 V (Li/Li⁺) using a charge-discharge system ZRU 50mA-10V (NTC Buster) at current densities of 20–9600 mA g^{−1} (I(charge) = I(discharge)), which corresponded to 0.1 C–60 C-rates. The capacity values were calculated taking into account the content of active cathode material. Electronic conductivity (dc-conductivity) was determined by the two-probe method on a Z500 PRO impedance meter at room temperature using cylindrical pellets with a diameter of 5 mm and a height of 1 mm pressed at 500 MPa with silver electrodes. Dc-conductivity (σ_{dc}) was calculated with the use of Equation (2):

$$\sigma_{dc} = h / (R_{dc}S), \quad (2)$$

where h represents the height of pellets, S represents their cross-sectional area, and R_{dc} represents dc-resistivity of the sample. Electrochemical impedance spectra (EIS) and cyclic voltammetry curves were recorded using an Elins P-8NANO potentiostat equipped with an attachment for EIS registration.

3. Results and Discussion

3.1. Composition and Morphology

To confirm the polymerization of aniline on the LFP precursor particles, IR spectroscopy was used (Figure S1). The IR spectra of polymerization products exhibited bands typical for polyaniline: stretching vibrations of C–N bond (1305 cm^{−1}) and stretching modes of benzoic ring C–C and quinoid ring C=C (1496 and 1581 cm^{−1}, respectively). The band at 3400 cm^{−1} was attributed to stretching vibrations of N–H or O–H bonds formed due to protonation of nitrogen atoms during the synthesis and sorption of water from air [44,45]. The intensities of the bands attributed to vibrations of benzoic and quinoid rings were almost equal, suggesting formation of PANI in the emeraldine form. The emerald green color of products also confirmed emeraldine formation (Figure 1).

The XRD patterns of the prepared composites are shown in Figure 2a. In the case of composites of LFP with N-CNTs and N-CNPs, XRD patterns showed reflexes of olivine-type LiFePO₄ (Card No. 81-1173, PDF-2 database). When the LFP precursor was coated by polyaniline according to method I, the materials obtained after heat-treatment in an inert atmosphere were the mixture of two crystalline phases: olivine-type LiFePO₄ and Fe₂P₂O₇ (Card No. 72-1516) (Figure 2b). This is most likely due to the partial transition of lithium into the solution in an acidic medium during synthesis. When the LFP precursor was coated by polyaniline according to method II, the formation of a single-phase crystalline LiFePO₄

was observed (Figure 2b). The parameters of the orthorhombic unit cell of LiFePO_4 were $a = 10.319 \pm 3 \text{ \AA}$, $b = 6.006 \pm 2 \text{ \AA}$, and $c = 4.692 \pm 1 \text{ \AA}$. According to XRD data, N-doped carbon materials both prepared from PANI and using a CVD technique (N-CNTs and N-CNPs) were amorphous.

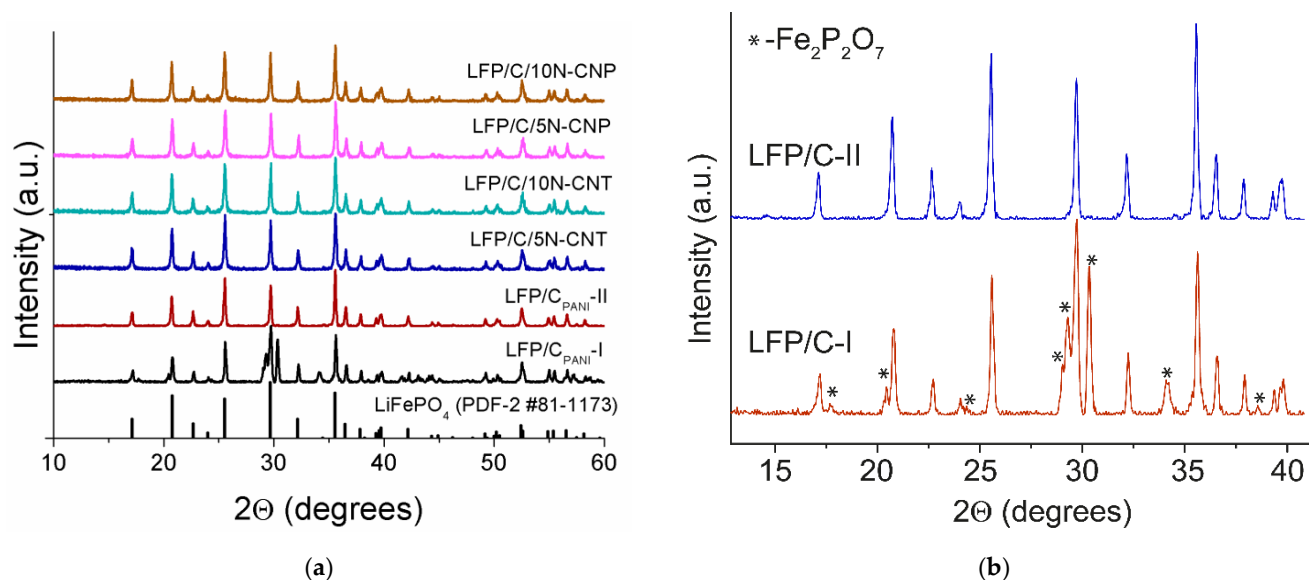


Figure 2. X-ray diffraction patterns of the composites: LFP/ $\text{C}_{\text{PANI-I}}$, LFP/ $\text{C}_{\text{PANI-II}}$, LFP/C/5N-CNT, LFP/C/10N-CNT, LFP/C/5N-CNP, and LFP/C/10N-CNP (a). Portions of XRD patterns of LFP/ $\text{C}_{\text{PANI-I}}$ and LFP/ $\text{C}_{\text{PANI-II}}$ in the region of $2\theta = 15\text{--}40^\circ$ (b).

In the case of LFP/ $\text{C}_{\text{PANI-II}}$ materials, the LFP crystallite size decreased from 65 to 44 nm with an increase in the initial ANI/LFP molar ratio from 0.125 to 1. The carbon content in these composites naturally increased after PANI carbonization. Since carbon is electrochemically inactive in the cathode material, it is desirable to minimize its content in LFP/C. The ANI/LFP molar ratio equal to 1 was chosen as the optimal one, as it results in the nanosize of electrode material particles and sufficiently high conductivity of LFP/ $\text{C}_{\text{PANI-II}}$ (Table 1, Figure S2). The LiFePO_4 crystallite size in the composites prepared using N-CNTs or N-CNPs and sucrose as a carbon source turned out to be somewhat larger (Table 1, Figure S2). This was unexpected, especially considering the carbon content in these materials (it was a sum of carbon from sucrose and N-CNTs or N-CNPs). Apparently, unlike polyaniline, sucrose and N-doped carbon materials are unevenly distributed over LFP precursor particles and cannot effectively prevent their growth during final annealing.

Table 1. Crystallite size, contents of carbon and nitrogen, electronic conductivity, and specific surface area of the prepared composites.

Sample	Crystallite Size, nm	Content, wt. %		Electronic Conductivity, S/cm	Specific Surface Area, m^2/g
		C	N		
LFP/C	75	4.7	-	4.6×10^{-7}	35
LFP/ $\text{C}_{\text{PANI-II}}$ (molar ratio ANI: LFP = 1)	44	5.0	0.5	4.0×10^{-5}	103
LFP/C/5N-CNT	61	9.8	0.2	8.6×10^{-3}	48
LFP/C/10N-CNT	57	14.3	0.4	1.8×10^{-2}	57
LFP/C/5N-CNP	62	9.3	1.1	1.3×10^{-5}	49
LFP/C/10N-CNP	54	13.1	1.8	4.1×10^{-5}	60

Figure S3 show the morphology of the prepared composites as well as the N-doped carbon nanomaterials used. N-doped CNTs formed large agglomerates of carbon nanotubes,

the outer diameter of which was 10–20 nm (Figure S3a). N-CNPs appeared as spherical and ovoid particles with the size of 50–200 nm, forming agglomerates (Figure S3b). Agglomerates of N-CNTs and N-CNPs remained in the composites even after their thorough grinding with the LFP precursor (Figure S3c–j). In the backscattered electron images, they appeared as darker areas since carbon has a lower atomic number than does Fe, P, and O (Figure S3d,f,h,j). According to SEM data, the particle size of LiFePO_4 in the composites was much larger than 44–62 nm (crystallite size estimated on the base of XRD reflex broadening), indicating that the LFP primary particles were agglomerated. This agglomeration was especially noticeable for the LFP/ $\text{C}_{\text{PANI-II}}$ sample (Figure 3a,b). To determine the primary particle sizes, the LFP/ $\text{C}_{\text{PANI-II}}$, LFP/C/5N-CNT and LFP/C/5N-CNP were analyzed by TEM (Figure S4). It can be seen that in the case of the LFP/ $\text{C}_{\text{PANI-II}}$ sample, carbon coated the surface of LFP particles and filled the intergranular spaces between them. In the case of LFP/C/5N-CNT and LFP/C/5N-CNP, LFP particles were distributed among carbon nanotubes and nanoparticles, respectively. The diameters of LFP particles were 35–58, 40–75, and 50–70 nm for LFP/ $\text{C}_{\text{PANI-II}}$, LFP/C/5N-CNT, and LFP/C/5N-CNP, respectively. This is rather consistent with the results of the XRD reflex broadening analysis (Figure S2, Table 1). According to EDS data, the content of Fe, P, and O in the composites prepared practically corresponded to the composition LiFePO_4 . In the LFP/ $\text{C}_{\text{PANI-II}}$ composite, the element mapping of nitrogen and carbon showed that they were uniformly distributed with the same shape (Figure 3c), indicating that N heteroatoms were included in carbon coating. Since it is not possible to estimate the C content correctly from EDS data because of carbon scotch used in SEM experiment, the N/C ratio was determined from the CHNS-analysis data. It was about 0.1, 0.03, and 0.17 for the LFP/ $\text{C}_{\text{PANI-II}}$ composite, N-CNTs, and N-CNPs, respectively. For the LFP composites with N-CNTs (N-CNPs), contents of carbon and nitrogen are listed in Table 1. As expected, the lowest N/C ratio was found for the composites with N-CNTs.

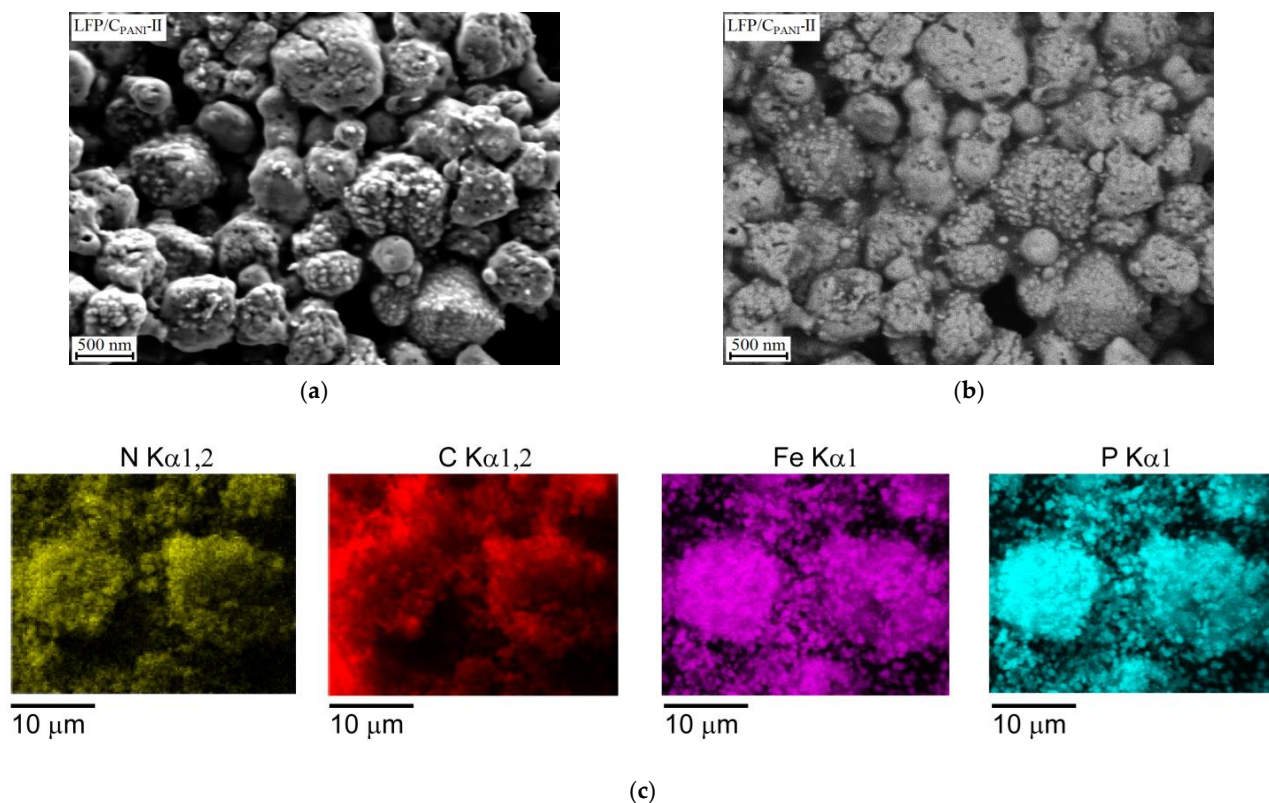


Figure 3. SEM images of LFP/ $\text{C}_{\text{PANI-II}}$ in the secondary (a) and backscattered (b) electrons; element mapping of LFP/ $\text{C}_{\text{PANI-II}}$: N, C, Fe, and P (c).

For the composites prepared, specific surface areas are listed in Table 1. The LFP/C_{PANI}-II composite had the highest specific surface area (103 m²/g) among the composites prepared. This is consistent with the lower crystallite size of LiFePO₄ in LFP/C_{PANI}-II. Despite a higher specific surface area of N-CNTs compared to N-CNPs (287 and 182 m²/g, respectively), the corresponding specific surface areas of the composites were almost the same. This may be due to the agglomeration of N-CNTs and/or the formation of coordination bonds between the LFP surface and the N-CNT polar groups.

When the studied composites were heated in air, oxidation of iron and N-doped carbon coating (carbon nanomaterials) occurred, accompanied by the release of carbon dioxide and nitrogen oxides. These processes are described in more detail using the LFP/C_{PANI}-II composite as an example (Figure 4). During its heating in air, a weight loss was observed at temperatures 25–200 °C due to the elimination of H₂O molecules adsorbed on its surface (Figure 4). Upon heating above 300 °C, the oxidation of polyaniline proceeded, and CO₂, NO, and NO₂ were formed according to mass spectrometry data (M/z = 44, 30, and 46). This was unexpectedly accompanied by an increase in the sample weight, which occurred in temperatures up to 390 °C. The reason for this nontrivial effect was a predominant adsorption of formed carbon oxide on the LFP surface, which has basic nature due to the lithium presence [21]. At further heating, an intensive PANI oxidation occurred, the products of which were no longer sorbed by the phosphate surface (the volume of gaseous products was too large, and they flew away without being sorbed). When LFP/C_{PANI}-II was heated above 500 °C, an increase in the sample weight was again observed due to the LFP oxidation. According to the XRD data, heating LFP above 500 °C resulted in the oxidation of Fe²⁺ and the formation of Fe₂O₃ and Li₃Fe₂(PO₄)₃ [46]:

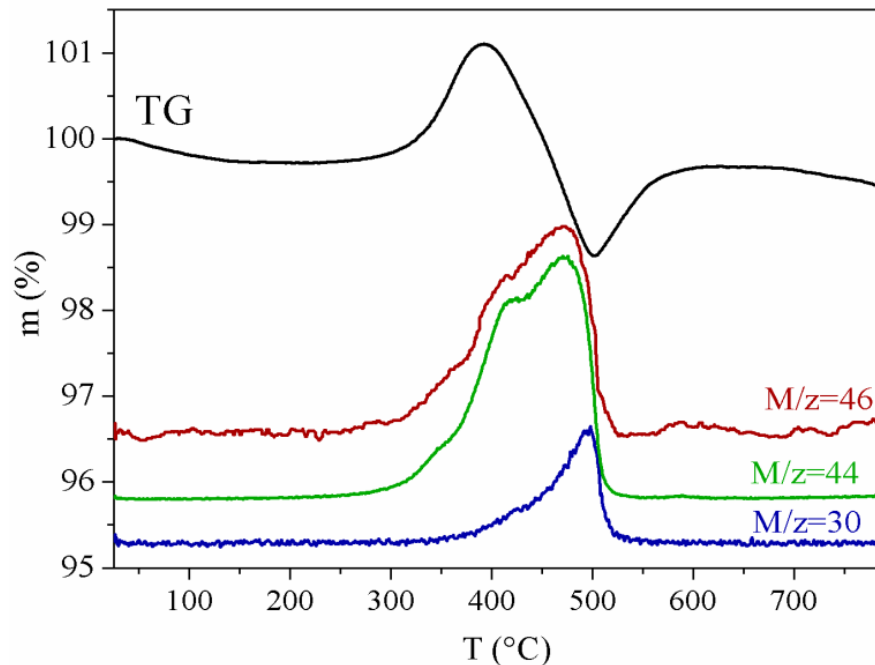
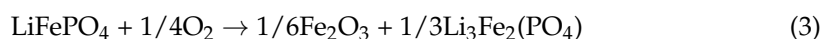


Figure 4. Thermogravimetric curve (TG) and ion currents with numbers (M/z) 46, 44, and 30 vs. the temperature for LFP/C_{PANI}-II.

Raman spectra of N-CNTs, N-CNPs, and C_{PANI} showed two intense bands at 1590 and 1350 cm^{−1} (Figure 5). This can be attributed to the G-band of graphite-like structure (sp²-hybridized carbon) and the D-band of disordered graphite, respectively [47,48]. In addition to these bands in the Raman spectra of N-CNPs and C_{PANI}, there appeared two peaks at ~1200 and ~1500 cm^{−1} (Figure 5), corresponding to vibrations of carbon in sp³-

hybridization [47]. The contributions of these additional peaks were 16, 22, and 47% for N-CNTs, C_{PANI}, and N-CNPs, respectively. Thus, N-CNTs and C_{PANI} coating were mainly represented by graphitic carbon, which is characterized by high conductivity [49]. This was in agreement with the results of the dc-conductivity measurements (Table 1, Figure S2), according to which the LFP/C/5N-CNT and LFP/C/10N-CNT samples exhibited the highest dc-conductivity, while the composites with N-CNPs showed the lowest.

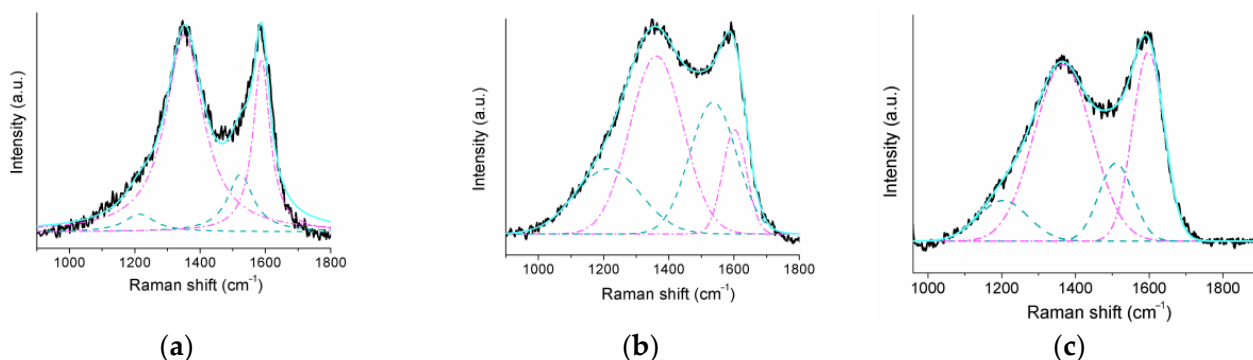


Figure 5. Raman spectra of (a) N-CNTs, (b) N-CNPs, and (c) the LFP/C_{PANI}-II. The dotted lines show the spectral curve fitting.

3.2. Electrochemical Properties

Figure 6 shows the charge–discharge curves of all the prepared LFP/C composites. Their shapes are almost identical and are typical for LiFePO₄-based cathodes. The charge–discharge profiles have a plateau, which corresponds to the Fe²⁺ ↔ Fe³⁺ transition at the potential of ~3.4 V. At a low charge–discharge rate, the discharge capacities of all the composites (except LFP/C and LFP/C/5N-CNP) are close to 167 mAh g^{−1}, while the theoretical capacity of LFP is 170 mAh g^{−1} (Figure 6a). It should also be noted that all the materials (except LFP/C/5N-CNP) were characterized by low polarization. For example, for the LFP/C_{PANI}-II, the difference between the average charge and discharge was about 0.04 V. This was even lower when compared with a similar LFP/C produced using a sol–gel technique with sucrose as a carbon source, for which $E_{\text{charge}} - E_{\text{discharge}} = 0.06$ V and even more so for LFP/C/5N-CNP (Figure 6a).

At low charge–discharge rates (≤ 400 mA g^{−1}), the values of the discharge capacity for all the composites were comparable to each other (Figures 6 and 7). Discharge capacities of the composites decreased with the increase in current density. This occurred much faster for the LFP composites with N-CNPs since the crystallite size of LFP in them was relatively large (Table 1), and N-doped carbon nanoparticles were distributed unevenly, forming agglomerates rather than continuous conducting pathways (Figure 3g–j). At high charge–discharge rates, the LFP/C_{PANI}-II showed the highest discharge capacity (96, 73, and 47 mAh g^{−1} at 5, 20, and 60 C, respectively). This, as well as a lower polarization of LFP/C-II, were due to a number of reasons, with a small crystallite size of LFP (Table 1) being one of them. A small crystallite size of LFP was determined by the limitation of the volume of growing particles by the carbon coating formed during the polyaniline decomposition. This led to a reduction in the diffusion length for Li⁺ and electrons to (from) grain boundaries during charge (discharge) [43]. Moreover, a high nitrogen content in carbon coating contributed to an increase in its conductivity and better interaction with LFP particles due to the formation of polar fragments in the carbon coating caused by the higher electronegativity of nitrogen compared to carbon [22]. The capacities of the LFP/C/5N-CNT and LFP/C/10N-CNT were lower than expected. This might have been due to the fact that N-CNTs were agglomerated in these composites (Figure 3c–f).

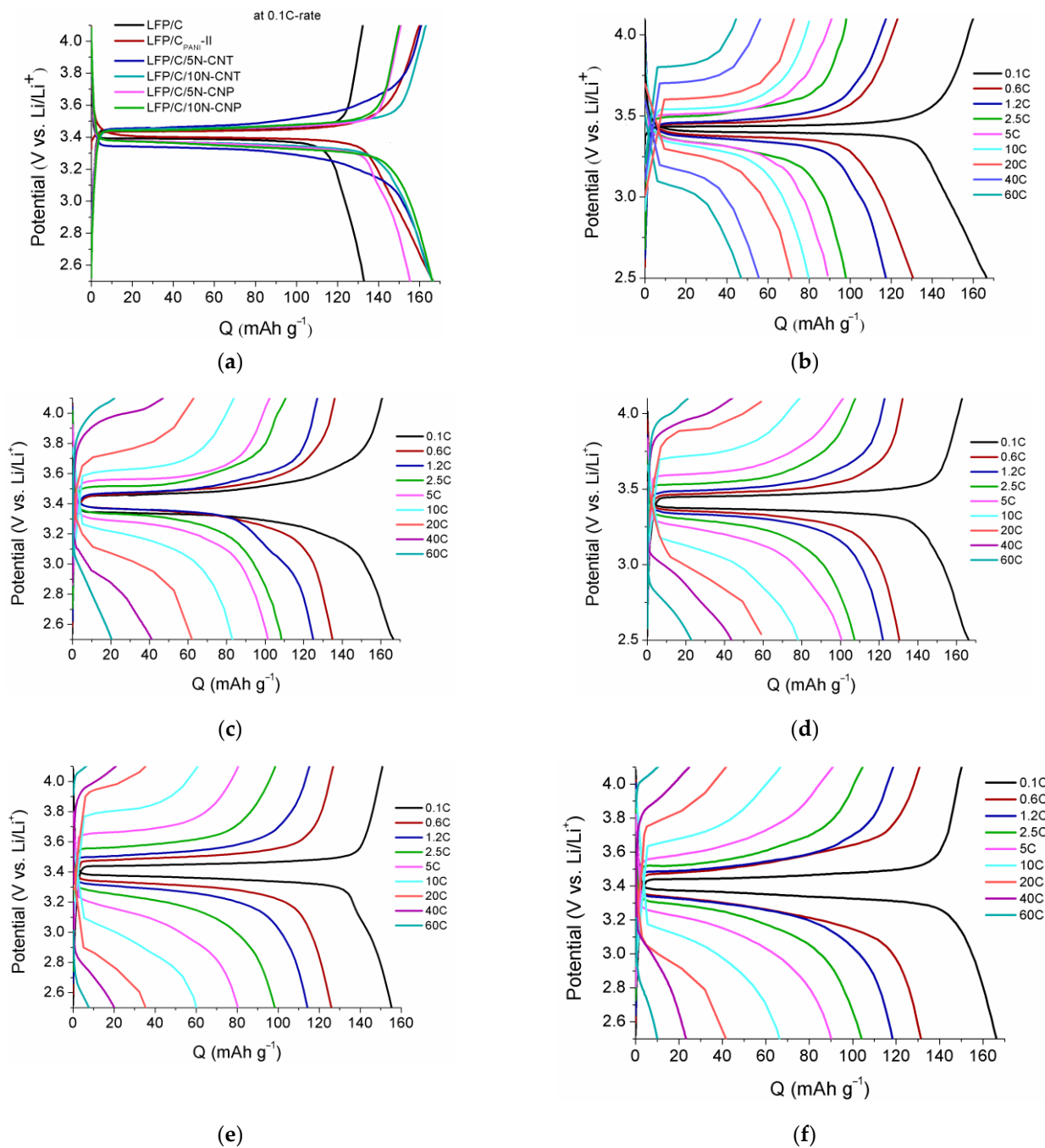


Figure 6. Initial charge–discharge curves of all the samples at a 0.1 C-rate (a), charge–discharge profiles at various C-rates for LFP/C_{PANI-II} (b), LFP/C/5N-CNT (c), LFP/C/10N-CNT (d), LFP/C/5N-CNP (e), and LFP/C/10N-CNP (f).

Figure 7b shows the long-term cycling performances of the LFP-based composites at a 0.6 C-rate. There was no significant capacity decay in any of the samples. The cycling stability was evaluated as the average discharge capacity loss per one cycle with the following equation:

$$\text{Cycling stability} = (Q_1 - Q_{100}) / (100 \times Q_1) \times 100\%, \quad (4)$$

where Q_1 and Q_{100} represent the discharge capacities at the 1st and 100th cycles, respectively. At a 0.6 C-rate, the average capacity loss per cycle was 0.023, 0.10, 0.045, 0.028, and 0.079% for LFP/C_{PANI-II}, LFP/C/5N-CNT, LFP/C/10N-CNT, LFP/C/5N-CNP, and LFP/C/10N-

CNP, respectively. These results prove that LFP/C_{PANI-II} has an excellent electrochemical performance.

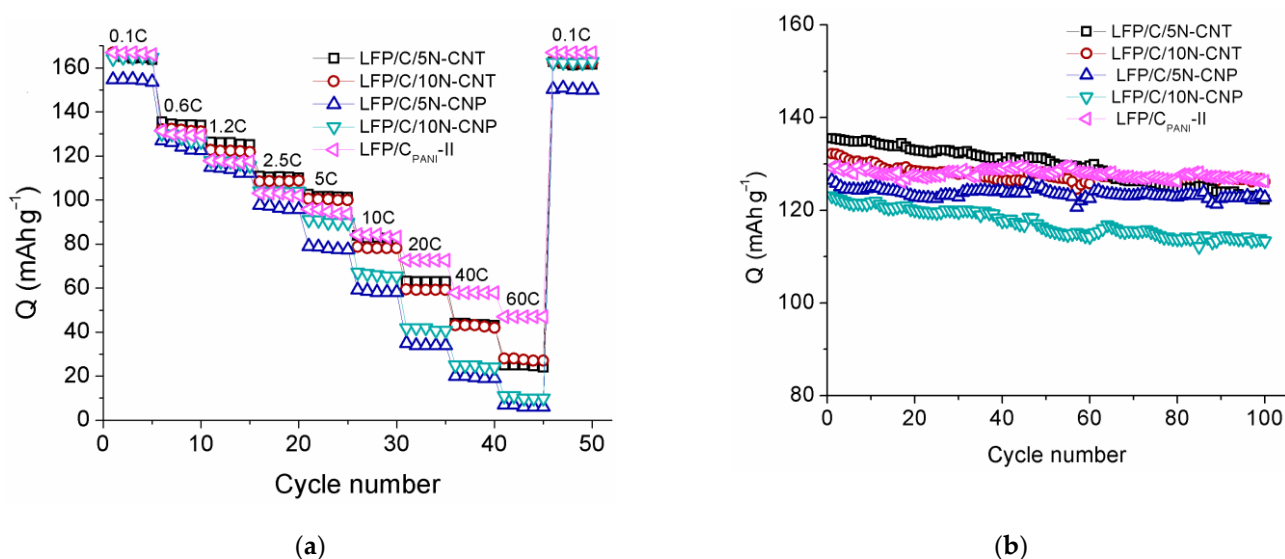


Figure 7. Change of discharge capacity during cycling of LFP/C/5N-CNT, LFP/C/10N-CNT, LFP/C/5N-CNP, LFP/C/10N-CNP, and LFP/C_{PANI-II} (a) and their long-term cycling performance at a 0.6 C-rate (b).

The discharge capacities of materials manufactured in this work exceed those of LFP/C materials coated with undoped carbon prepared using sucrose or glucose and are comparable, as a whole, with discharge capacities of materials prepared using PANI as a source of carbon coating or N-doped CNTs (Table 2). Capacities of some LFP/C materials reported in the literature are somewhat higher than those obtained in this work. Most of these results are related to LFP composites made with graphene (Table 2). For example, owing to the synergy of CNTs and graphene, LiFePO₄/C prepared with them hydrothermally exhibits an outstanding rate capability (103 mAh g⁻¹ at 40 C) [50].

Table 2. Comparison of electrochemical performances of LFP/C composites.

Cathode Composition	LFP Synthesis Method	Carbon Source	LFP, wt. %	Capacity at C-Rate, mAh g ⁻¹						Ref.
				0.1 C	1 C	5 C	10 C	20 C	≥30 C	
LFP/C	sol-gel	PANI	95	167	114	96	84	73	47	this work
LFP/C/N-CNT		N-doped CNTs, sucrose	91	166	126	102	84	63	25 (56 C)	
LFP/C	sol-gel	Sucrose	95	136	105	65	-	-	-	[10]
LFP/C	solvothermal	Glucose	86	147	111	73	-	-	-	[51]
LFP/C	solid state reaction	PANI-Cl	82.6	163	148	-	100	-	-	[35]
LFP/C	carbothermal reduction	PANI, sucrose	-	164	140	50	5	-	-	[38]
LFP/N-CNT	sol-gel	N-doped CNTs	89	138	110	68	48	-	-	[52]
LFP/N-CNT	freeze-drying	N-doped CNTs	88.5	158	143	103	71	-	-	[20]
LFP/G/CNT	hydrothermal	Graphene, CNT	95	168	155	133	120	113	103 (40 C)	[50]
LFP/C/G	high-energy ball milling/solid state reaction	Glucose, graphene	97	164	147	127	112	81	-	[53]
LFP/C/NG	hydrothermal	N-doped graphene, glucose	92	156	129	105	88	-	-	[40]
LFP/NG	hydrothermal	N-doped graphene	95	163	157	136	114	-	-	[41]

As reported in the literature, carbon coating of LFP using PANI can be produced either by the aniline polymerization in the presence of FePO₄ and is followed by its annealing with lithium salt and sucrose in an inert atmosphere or via the solid-state

reaction using a previously prepared PANI [35,36]. In this work, a novel simple method for ANI polymerization in the presence of LFP precursor was developed. Simplicity and high performance at low carbon content can be included among its advantages. The introduction of a carbon source (PANI) before final annealing procedure prevents particles from agglomeration and promotes a material with smaller particles, which contribute to higher capacities especially at high discharge–charge rates.

Figure 8 presents the cyclic voltammetry curves of the LFP/C_{PANI-II}, LFP/C/5N-CNT, LFP/C/10N-CNT, LFP/C/5N-CNP, and LFP/C/10N-CNP at various scan rates from 0.1 to 3.2 mV/s. The redox peaks in the anodic and cathodic regions were assigned to the $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ redox reaction. Both cathodic and anodic peaks in the CV curve of the LFP/C_{PANI-II} appear to be higher than those of other samples. Moreover, the LFP/C_{PANI-II} shows the lowest peak potential differences (ΔE) at all potential sweep rates, indicating the lowest electrode polarization (reversibility) and an improved electrochemical kinetics (Figure 8f). For example, at 0.8 mV s^{−1}, ΔE are 320, 640, 470, 523, and 539 mV for LFP/C_{PANI-II}, LFP/C/5N-CNT, LFP/C/10N-CNT, LFP/C/5N-CNP, and LFP/C/10N-CNP, respectively. This agrees well with the results of the charge–discharge testing. The LFP/C/5N-CNT sample exhibits the lowest reversibility indicating the lowest “binding” of the LFP particles among these composites.

The Nyquist plots for the LFP/C_{PANI-II}, LFP/C/5N-CNT, LFP/C/10N-CNT, LFP/C/5N-CNP, and LFP/C/10N-CNP are shown in Figure 9a. The impedance spectra consist of the following two parts: a semicircle and an inclined line in the high/medium and the low-frequency region, respectively. This is due to the charge transfer resistance and the diffusion of Li^+ , respectively. The high-frequency semicircle is associated with the charge transfer resistance (R_{ct}) at interfaces between the active material particles and an electrolyte, and a sloping line is responsible for the diffusion of lithium and corresponds to the Warburg impedance. The diffusion coefficient of lithium ions (D_{Li}) can be calculated from Equations (5) and (6):

$$Z' = W_c \times \omega^{-1/2} + R_{\text{ct}}, \quad (5)$$

$$D_{\text{Li}} = 1/2R^2 \times T^2(S \times n^2 \times F^2 \times W_c \times C_{\text{Li}})^{-2}, \quad (6)$$

where Z' represents the real part of the impedance; W_c , the Warburg coefficient; ω , the angular frequency; T , the absolute temperature; R , the ideal gas constant; S , the electrode surface area; n , the number of e^- transferred; F , the Faraday constant; and C_{Li} , the concentration of lithium ions. The Warburg coefficient is the slope of the fitted line of Z'' vs. $\omega^{-1/2}$ plots in the low frequency region (Figure 9b) and can be estimated from Equation (5). The diffusion coefficients of lithium ions calculated according to Equation (6) were 1.2×10^{-13} , 5.8×10^{-14} , 9.5×10^{-14} , 8.8×10^{-14} , and 1.0×10^{-13} cm²/s for the LFP/C_{PANI-II}, LFP/C/5N-CNT, LFP/C/10N-CNT, LFP/C/5N-CNP, and LFP/C/10N-CNP, respectively. The LFP/C_{PANI-II} had the highest D_{Li} , which was associated with a more uniform C_{PANI} coverage of the LFP particles and led to the excellent electrochemical characteristics and cyclic stability of this material.

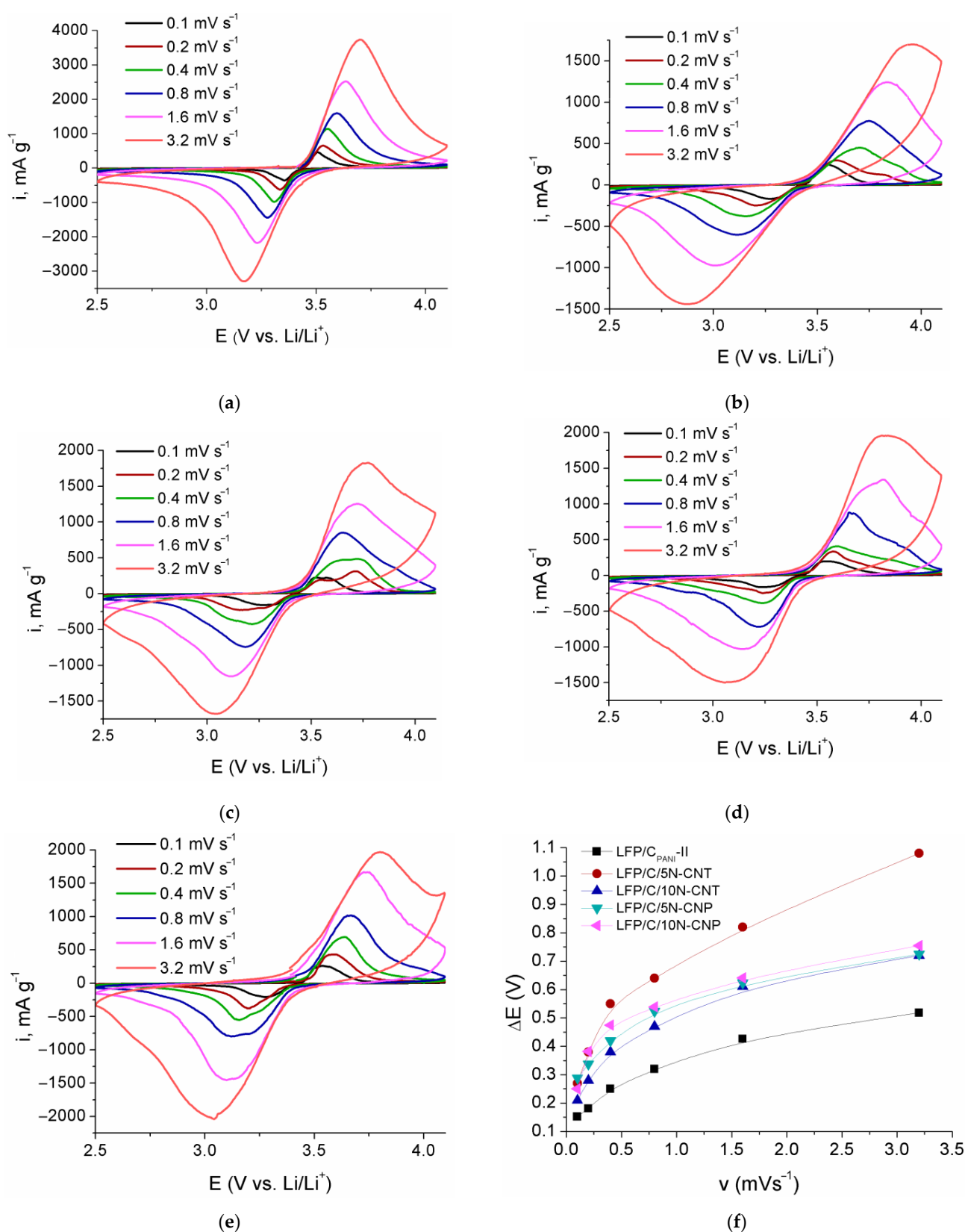


Figure 8. Cyclic voltammetry curves for the LFP/C_{PANI-II} (a), LFP/C/5N-CNT (b), LFP/C/10N-CNT (c), LFP/C/5N-CNP (d), and LFP/C/10N-CNP (e); the peak potential differences for these composites (f).

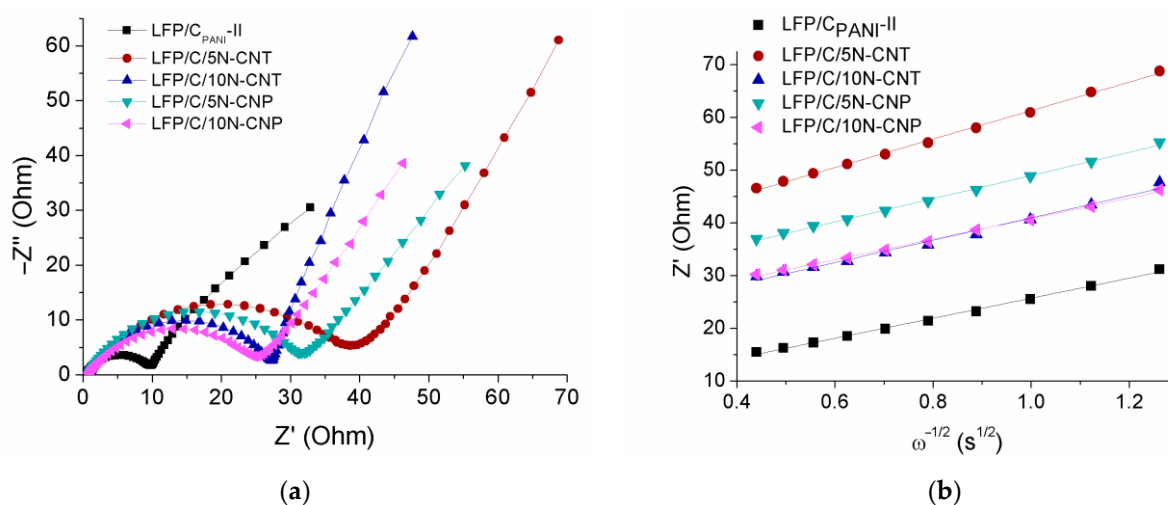


Figure 9. Electrochemical impedance spectroscopy data: the Nyquist plots (a) and the fitting plots of Z' vs. $\omega^{-1/2}$ (b).

4. Conclusions

In this work, the effects of different nitrogen-doped carbon additives (carbon coating from polyaniline, N-doped carbon nanotubes, and N-doped carbon nanoparticles) on the electrochemical properties of LiFePO_4 composites were studied. Moreover, a simple procedure for preparation of composite materials based on LFP and N-doped carbon from PANI was developed. All the composites show increased electronic conductivities and rate capability due to the presence of highly conductive carbons doped with nitrogen atoms providing effective pathways for electrons and Li^+ . During pyrolysis, polyaniline limits the growth of LFP particles better than does sucrose. N-doped carbon nanomaterials (CNTs and CNPs) were largely agglomerated which, combined with the larger LFP particles in the composites, resulted in a worse rate capability than that of the $\text{LFP/C}_{\text{PANI-II}}$ nanocomposite, the discharge capacities of which were 167, 111, 96, 84, 73, and 47 mAh g^{-1} at 0.1, 1.2, 5, 10, 20, and 60 C-rates, respectively.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/batteries8120256/s1>, Figure S1: FTIR spectra of the pristine LFP precursor and the LFP precursor/PANI composite; Figure S2: The radar charts with the comparison of the crystallite size, contents of carbon and nitrogen, electronic conductivity, and specific surface areas of the prepared composites; Figure S3: SEM images of N-CNTs (a), N-CNPs (b), the LFP/C/5N-CNT (c, d), the LFP/C/10N-CNT (e, f), LFP/C/5N-CNP (g, h), and LFP/C/10N-CNP (i, j): in secondary (a–c, e, g, i) and backscattered (d, f, h, j) electrons; Figure S4: TEM images of the LFP/C_{PANI-II} (a), LFP/C/5N-CNT (b), LFP/C/5N-CNP (c).

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