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Magnifying the GCD behaviour of $FePO_4$ composite with low temperature plasma exposed Bamboo charcoal enforced in energy storage devices

ABSTRACT

Materials based on phosphate have been suggested as suitable electrode components for energy storage devices and also indicated that the phosphate framework can help to keep active sites stable. The physical and chemical properties of Fe-based phosphates make them promising cathode compounds for energy storage systems. In this work, the additive carbonous material as a bamboo charcoal (BCC) which was prepared and activated using the pyrolysis process. The irradiation of DC glow discharge plasma improved the surface attributes such as wettability, adhesion, and conductivity. Here, the hydrothermal technique was used to synthesize $FePO_4$ *nano particles. The dielectric behaviour was analysed at room temperature for pure* $FePO_4$ *and composite of* $FePO_4$*/Plasma treated BCC. The GCD behaviour of pure* $FePO_4$ *and composite of* $FePO_4$*/Plasma treated BCC was analysed with aqueous electrolyte of 2M KOH at different current densities. In perspective, the dielectric constant and specific capacitance of the* $FePO_4$*/plasma treated BCC material seems to be very strong.*

Key words: *Bamboo charcoal (BCC),* $FePO_4$ *nano particles, DC glow discharge plasma, Surface modification, GCD, dielectric properties etc.*

1. INTRODUCTION

The primary goal of the endeavour is to build phosphate-based cathodes that are both affordable and highly effective in energy storage applications with the addition of DC glow discharge plasma exposed bamboo charcoal(BCC). The high theoretical specific capacity and improved electrochemical reversibility of iron phosphate ($FePO_4$) have made it a highly preferred cathode material for batteries [1,2]. It has a high cell voltage (approximately 3 V) which is powered by PO_4^{3-} and results in a modest fermi coefficient of the Fe^{3+}/Fe^{2+} redox during discharge [3,4]. It also demonstrates a significant hypothetical energy storage of 178 mAh/g [5,6]. Nevertheless, some rare elements, such as Ni, Co, and V, are not suited for use as electrode materials in large-scale energy storage due to ecological and environmental concerns .But in contrast, Fe is significantly more prevalent on Earth and much less expensive. Fe-based materials have drawn a lot of interest in their development as affordable and secure cathode materials [7]. The phosphate framework is capable of stabilising active sites in metal phosphate, and $FePO_4$ has excellent physical and chemical properties, allowing it to be used in batteries which include lithium-ion and sodium-ion batteries [8]. $FePO_4$ has been reported as a potential cathode component for sodium storage due to its good redox reversibility and large theoretical capacity [9,10]. However, as a result of the Na^+ insertion/extraction operations, it exhibits a notable volumetric shift of over 22% and produces low electronic conductivity, which results in unpredictable cyclic performance and poor rate capacity [11,12]. Effective nano-architecture designs and carbon decorating are two viable solutions for resolving the aforementioned issues and thereby improving electrochemical characteristics [13-16]. In this research, the carbon material is activated bamboo charcoal. Since BCC has the highest porosity and the lowest density of all natural woods, researchers have been concentrating on using it as reinforcement in a variety of fields [17-19]. It also has the highest thermal, chemical, mechanical, and electrical stability. DC glow discharge plasma is a powerful method for altering surface characteristics like wettability, surface area, number of pores and adhesion without changing the material's composition [20].

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Activated bamboo charcoal that has been synthesised by the pyrolysis technique which is subjected to the exposure of DC glow discharge plasma for surface modification as a way to increase the discharge duration .Free radicals are produced as a result of plasma activity and can act as interaction points for reactive species (polar groups), increasing the surface wettability and improving adhesion quality, which is essential for making a well-incorporated composite. Added improvements were made to additional surface characteristics like surface area and number of pores on the surfaces. In this study, plasma-exposed BCC is well embedded with hydrothermally synthesised $FePO_4$ nanoparticles, which exhibit enhanced structural, morphological, and electrochemical behaviour compared to pure $FePO_4$. During plasma exposure to BCC, more pores on the surface of the BCC developed, but the existing pores remained unaltered.

2. MATERIALS AND METHODS

The used precursors, synthesis of $FePO_4$, synthesis of composite $FePO_4$/plasma exposed BCC, Characterization methods, Plasma treatment and electrode preparation were reviewed in the journal [9,21].

3. RESULTS AND DISCUSSION

3.1. Structural analysis

The exact phase structure is in agreement with JCPDS: (96-901-2513), which explicitly describes the phase composition of $FePO_4$ and figure (1) shows the crystallographic structure of $FePO_4$.

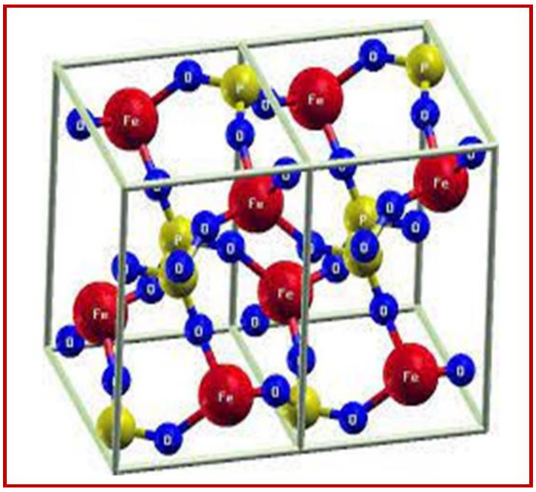


Figure 1. Crystallographic structure of $FePO_4$

Slika 1. Kristalografska struktura $FePO_4$

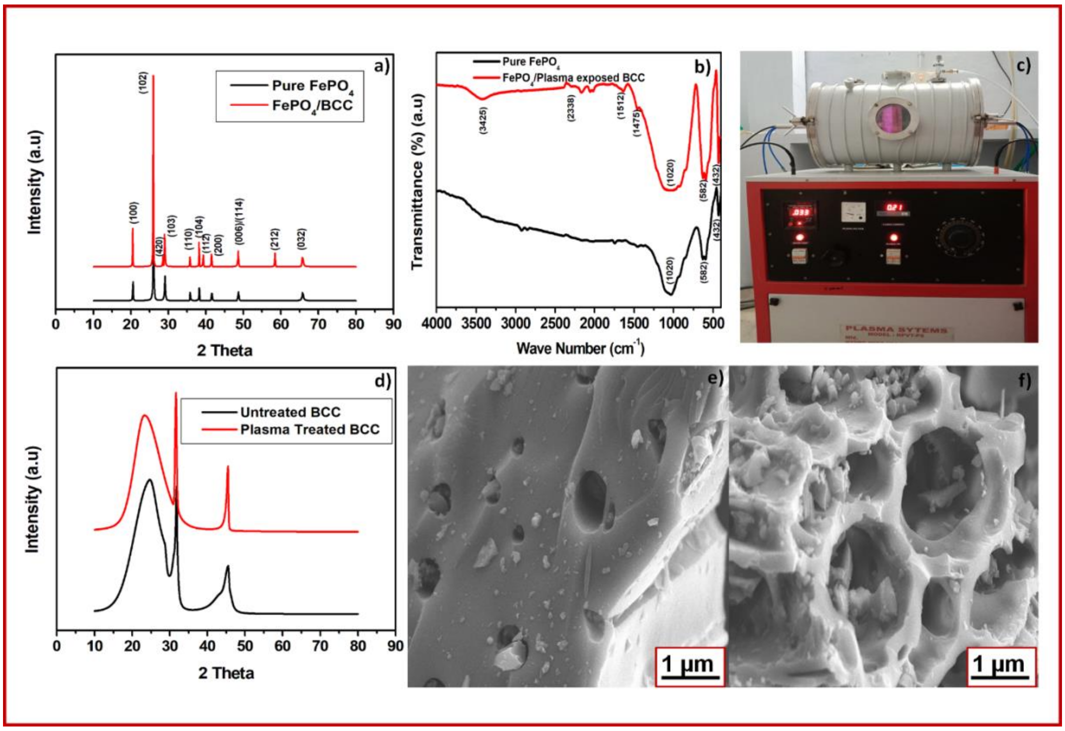
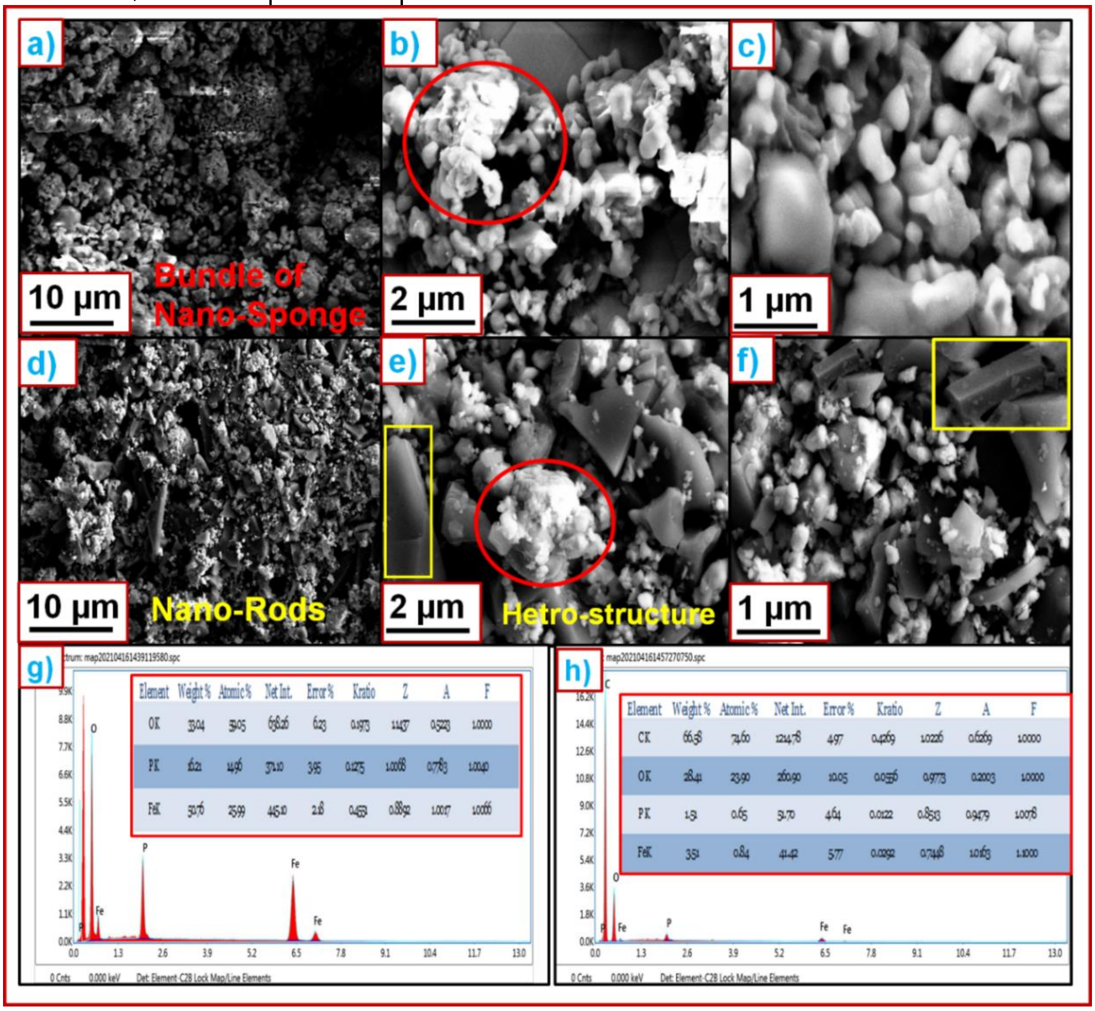


Figure 2. (a) XRD pattern of pure $FePO_4$ and $FePO_4$ / Plasma exposed BCC, (b) FTIR pattern of pure $FePO_4$ and $FePO_4$ / Plasma exposed BCC (c) View of Cold Plasma Chamber (d) XRD Analysis of untreated and plasma treated BCC (e) FESEM image of untreated BCC (f) FESEM image of Plasma treated BCC

Slika 2. (a) XRD uzorak čistog $FePO_4$ i $FePO_4$ / BCC izložen plazmi (b) FTIR uzorak čistog $FePO_4$ i $FePO_4$ / BCC izloženog plazmi (c) Pogled na komoru hladne plazme (d) XRD analiza netretiranog i plazmom tretiranog BCC (e) FESEM slika netretiranog BCC (f) FESEM slika BCC tretiranog plazmom

Figure 2(a) shows the crystallographic structure of both $FePO_4$ and $FePO_4$/plasma processed BCC substances. Figure 2 (d) depicts the XRD structure of Plasma untreated and treated BCC. In structural analysis the intensity of composite $FePO_4$/plasma-treated BCC was raised without changing its original character, and it has sharper diffraction peaks than pure $FePO_4$ nanoparticles.

The presence of additional carbon peaks indicates that plasma-exposed BCC were well incorporated into the interface of $FePO_4$ nanoparticles. The appearance of $FePO_4$ can be seen in the peaks at 1020, 582, 630, and 432 cm^{-1} in the $FePO_4$/plasma exposed BCC composite plot reveals in the figure 2(b). Additionally, a novel absorption peak in the C=C stretching mode was discovered at 1475 cm^{-1}, confirming that the plasma-exposed BCC reacted with the interior lattices of $FePO_4$. Due to plasma exposure on BCC, elevated O-H stretching occurs at 1515 cm^{-1} and 3425 cm^{-1}. When comparing the collected spectra, it can be seen that the $FePO_4$/plasma-treated BCC has a higher absorption properties than the pure $FePO_4$, which means that the stretching vibrations are much clearer in the composite. Furthermore, the presence of more OH-Carboxylic groups on the surface of the composite indicates that wettability has been improved and the surface has shifted from hydrophobic to hydrophilic. This FT-IR spectrum demonstrates that the material is a Phosphate group. The figure 3(a-f) depicts the morphological features of bare $FePO_4$ and $FePO_4$ / plasma exposed BCC. The composite material has hetero-structure morphology like bundle of sponge $FePO_4$ embedded with Plasma treated carbon nano rods which increases the ion transportation between the active material and electrolyte.



g)

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
OK	33.04	59.05	638.26	6.23	0.1973	1.1437	0.5223	1.0000
PK	16.21	14.96	371.10	3.95	0.1275	1.0068	0.7783	1.0040
FeK	50.76	25.99	445.10	2.18	0.4531	0.8892	1.0017	1.0066

h)

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
CK	66.58	74.60	1214.78	4.97	0.4269	1.0226	0.6269	1.0000
OK	28.41	23.90	260.90	10.05	0.0556	0.9773	0.2003	1.0000
PK	1.51	0.65	51.70	4.64	0.0122	0.8513	0.9479	1.0078
FeK	3.51	0.84	41.42	5.77	0.0292	0.7448	1.0163	1.1000

Figure 3. FESEM analysis of pure $FePO_4$ and $FePO_4$/plasma exposed BCC (a-c) Bundle of pure $FePO_4$ (d-f) Hetero structure of bundle of nano sponge and nano rods of $FePO_4$/plasma exposed BCC (g) EDAX spectrum of Pure $FePO_4$ (h) EDAX spectrum of $FePO_4$/plasma exposed BCC

Slika 3. FESEM analiza čistog $FePO_4$ i $FePO_4$/BCC izloženog plazmi (a-c) Snop čistog $FePO_4$ (d-f) Hetero struktura snopa nano sunđera i nano štapića $FePO_4$ / izloženog plazmi BCC (g) EDAX spektar čistog $FePO_4$ (h) EDAX spektar od $FePO_4$ / BCC izloženog plazmi

The plasma treated samples have more porous and active sites which improves the electrochemical characteristic. The EDAX method was utilized to examine the presenting elements of Fe, P, O and C without any kind of impurities as shown in figure 3 (g-h).

3.2. Dielectric Studies

Nanostructured materials have better dielectric characteristics than regular bulk materials. Here the dielectric characteristics were investigated at frequencies ranging from 1 Hz to 5 MHz by using two probe method [22]

The dielectric constant is computed using the equation,

$$\varepsilon_r = \frac{C \times d}{\varepsilon_0 \times A} \qquad (1)$$

Where, A is the Area of the sample,d is the thickness of the sample, C is the parallel capacitance, ε_0 is the absolute permittivity of free space (8.859 10^{-12} F m^{-1})

Fig. 4 (a&b) displays the dielectric constant curve for samples of pure $FePO_4$ and $FePO_4$/plasma exposed BCC, respectively. The graph shows that the dielectric constant is relatively high in the low frequency and gradually declines with increasing applied frequency. This could be because of mixtures of all four polarisations, including space charge, orientation, electronic, and ionic polarisation. According to the dielectric measurements, the $FePO_4$/ plasma exposed BCC electrode material has a higher dielectric constant ratio than the pure $FePO_4$ electrode sample. In pure $FePO_4$,the dielectric constant decreased gradually with increasing applied electric frequency and it saturated at 1 Hz, but in composite the saturation happened at 3Hz which shows that the addition of plasma exposed BCC increased the sustainability of dielectric constant.

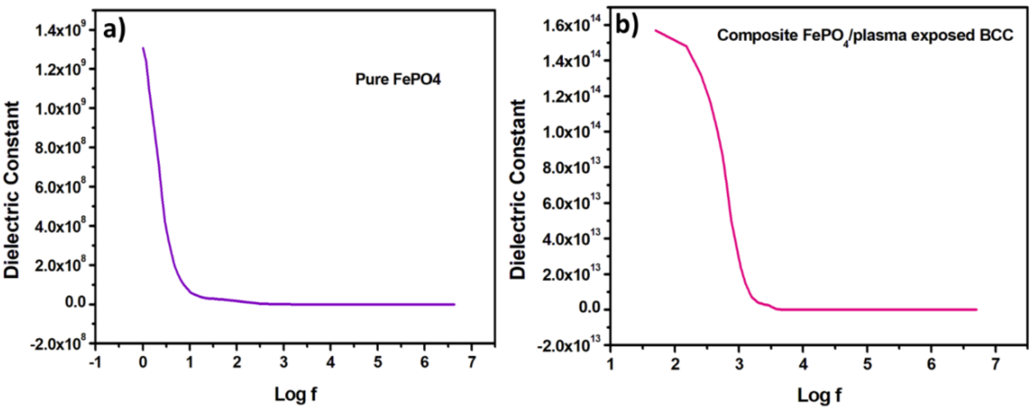


Figure 4. Dielectric analysis (a) Pure $FePO_4$ (b) Composite $FePO_4$/Plasma exposed BCC

Slika 4. Dielektrična analiza (a) Čisti $FePO_4$ (b) Kompozitni $FePO_4$ /plazma izložen BCC

3.3. Galvanostatic charge-discharge analysis

GCD (galvanostatic charge-discharge) is a supplementary method for determining specific capacitance under regulated current circumstances. Among two predetermined voltage points with a constant applied current, the energy storage device is charged and discharged. The discharge curves were used to compute specific capacitance using the following equation [23],

$$Csp = \frac{I*\Delta t}{\Delta V*m} \qquad (2)$$

where, I = applied current, Δt = discharge time, ΔV = voltage, and m = average mass of the active substance in the electrode.

These observations were performed with 2M concentration of KOH at voltages between 0 V and 0.4 V with different current densities ranging from 3 to 9 mA/g. Figures 5 (a&b) shows that the GCD profile for electrode samples made up of pure $FePO_4$ and $FePO_4$/ plasma exposed BCC. Specific capacitance values based on the GCD profile was revealed to be 585, 455, 398 and 337 F/g for pure $FePO_4$ and for $FePO_4$ / plasma exposed BCC the specific capacitance values are 1069, 738, 687 and 391 F/g with the current densities of 3, 5, 7 and 9 mA/g. The results show that the optimum capacitance value occurs at a minimum current density of 3 mA/g, while capacitance values reduced as current densities raised from 5 to 9 mA/g. According to the findings, the incorporation of plasma-exposed BCC greatly boosts the capacitance levels because the plasma influence surface features, especially adhesion, allowing it much simpler for it to interface with subsequent fabrication of the new materials and improving the active sites.

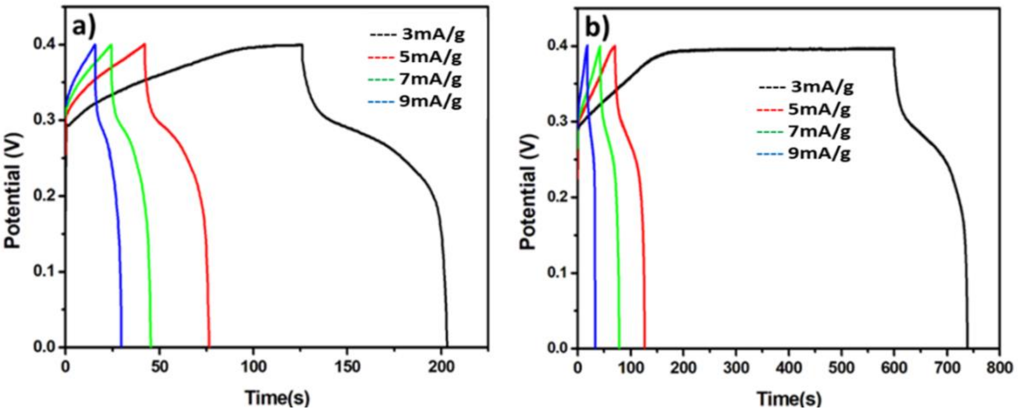


Figure 5. GCD profile (a) Pure $FePO_4$ (b) Composite $FePO_4$/Plasma exposed BCC

Slika 5. GCD profil (a) Čisti $FePO_4$ (b) Kompozitni $FePO_4$ /plazma izložen BC

4. CONCLUSION

To summarise, an aqueous hydrothermal and consequent annealing technique was used to successfully produce an integrated electrode of $FePO_4$/plasma exposed BCC. Analysis showed that the trigonal structure of $FePO_4$ nanoparticles was well incorporated with plasma exposed BCC. New functional groups are created during the plasma treatment in order to increase wettability and adhesion. After the addition of plasma-exposed BCC, the dielectric constant was significantly increased. The dielectric constant is greater at low frequencies and decreases with increasing frequencies. The increased dielectric constants should be related to the high charge build-up and interfacial polarisation at the massive interfaces of $FePO_4$ and plasma exposed BCC. Furthermore, the strong connectivity of $FePO_4$ with plasma exposed BCC, which is advantageous for the transmission continuity of polarisations, also contributes to the extremely high dielectric constants and the exposure of plasma causes this significant conjunction in composites by improving adhesion surface behaviour. This was caused by the change in surface characteristics from hydrophobic to hydrophilic. For pure $FePO_4$, the specific capacitance values were found to be 585, 455, 398, and 337 F/g and $FePO_4$/Plasma exposed BCC, the specific capacitance ranges are 1069, 738, 687, and 391 F/g with current densities of 3, 5, 7, and 9 mA/g based on the GCD profile. According to the GCD profile, the hybrid electrode has a greater specific capacitance as a result of the addition of highly porous BCC, which has better electrode/electrolyte contact area and abundant electro active sites, which improves charge-discharge behaviour. Overall, the hybrid $FePO_4$/plasma treated BCC electrode exhibits superior electrochemical behaviour compared to pure $FePO_4$ electrode. The findings suggest that the composite electrode demonstrated great accuracy and long-term stability, which may be more beneficial for high-performance battery applications.

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IZVOD

UVEĆAVANJE GCD PONAŠANJA KOMPOZITA $FePO_4$ SA BAMBUSOVIM UGLJEM IZLOŽENIM PLAZMI NISKE TEMPERATURE, PRIMENJENIM U UREĐAJIMA ZA SKLADIŠTENJE ENERGIJE

Materijali zasnovani na fosfatu su predloženi kao prikladne komponente elektrode za uređaje za skladištenje energije i takođe su ukazali da fosfatni okvir može pomoći da se aktivna mesta održe stabilnima. Fizička i hemijska svojstva fosfata na bazi Fe čine ih obećavajućim katodnim jedinjenjima za sisteme za skladištenje energije. U ovom radu je aditivni ugljeni materijal kao bambusov ugalj koji je pripremljen i aktiviran postupkom pirolize (BCC). Zračenje plazme DC sjajnog pražnjenja poboljšalo je atribute površine kao što su kvašenje, adhezija i provodljivost. Ovde je korišćena hidrotermalna tehnika za sintezu nanočestica $FePO_4$. Dielektrično ponašanje je analizirano na sobnoj temperaturi za čisti $FePO_4$ i kompozit BCC tretiran sa $FePO_4$/plazmom. GCD ponašanje čistog $FePO_4$ i kompozita BCC tretiranog $FePO_4$/plazmom je analizirano sa vodenim elektrolitom od 2M KOH pri različitim gustinama struje. U perspektivi, čini se da su dielektrična konstanta i specifična kapacitivnost BCC materijala tretiranog $FePO_4$/plazmom veoma jaki.

Ključne reči*: Bambusov ugalj (BCC), $FePO_4$ nano čestice, DC usijana plazma, modifikacija površine, GCD, dielektrična svojstva itd.*

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