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Synthesis and Electrochemical Characterization of B_4C-BN Nanocomposite Powders for New Generation Energy Storage Applications

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Abstract: The development of supercapacitors with high energy density, stability, and a wide range of operating potential is an urgent issue. To satisfy the required enhancements on supercapacitor modules, new-generation electrode materials need to be designed. In this study, B_4C-BN nanocomposite powder is proposed as a novel electrode material. Nanocomposite powders were synthesized via cost effective sol-gel technique and processing conditions were optimized to tailor phase ratio, particle size, and morphology. The phase composition of synthesized powders was characterized by XRD. The morphology of the particles was examined by SEM and HR-FESEM techniques. The electrochemical performance of electrodes was investigated by using cyclic voltammetry (CV). The results indicate that particle morphology, size, and the ratio of B_4C/BN phases have a considerable impact on electrochemical performance of fabricated electrodes.

Keywords: Sol-Gel, B_4C, BN, energy storage.

Yeni Nesil Enerji Depolama Uygulamaları İçin B_4C-BN Nanokompozit Tozlarının Sentezi ve Elektrokimyasal Karakterizasyonu

Özet: Yüksek enerji yoğunluğuna, stabiliteye ve geniş bir çalışma potansiyel aralığına sahip süperkapasitörlerin geliştirilmesi gereklidir. Süperkapasitör modüllerinde gerekli iyileştirmeleri sağlamak için yeni nesil elektrot malzemelerinin tasarlanması gerekmektedir. Bu çalışmada yeni bir elektrot malzemesi olarak B_4C-BN nanokompozit tozu önerilmiştir. Nanokompozit tozlar uygun maliyetli sol-jel tekniği kullanılarak sentezlenmiştir. Son ürün tozun faz oranı, parçacık boyutu ve morfolojisi sentez süreç parametreleri optimizasyonu ile kontrol edilmiştir. Sentezlenen tozların faz bileşimi XRD analizi ile karakterize edilmiştir. Parçacıkların morfolojisi SEM ve HR-FESEM teknikleriyle incelenmiştir. Elektrotların elektrokimyasal performansı çevrimsel voltametri (CV) kullanılarak araştırılmıştır. Sonuçlar parçacık morfolojisinin, boyutunun ve B_4C/BN fazlarının oranının, üretilen elektrotların elektrokimyasal performansını önemli ölçüde etkilediğini göstermektedir.

Anahtar Kelimeler: Sol-Jel, B_4C, BN, enerji depolama.

Article

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1.Introduction

Due to their distinct redox mechanism, materials such as metal sulfides, metal nitrides, and metal carbides, often referred to as pseudocapacitive or battery-type materials, have been extensively researched for their potential as supercapacitor electrodes (Sanger et al., 2016). Transition metal carbides like TiC, V_4C_3, WC, MoC, and B_4C have garnered significant interest due to their chemical stability (Liang et al., 2003).

Among these, boron carbide (B_4C) stands out as a lightweight refractory semiconductor and the third hardest material known at room temperature. It boasts numerous unique properties including high resistance to chemical corrosion, exceptional thermal stability, low density (~2.5 g cm^{-3}), minimal thermal expansion coefficient, high melting point (>2400 °C), notable Seebeck coefficient, and substantial neutron absorption cross-section (Avcıoğlu et al., 2020). The crystal structure of boron carbide is particularly distinctive, featuring a rhombohedral structure (R m, No. 166) comprising a B_{12} icosahedral unit and a C–B–C chain ($B_{13}C_2$ (B_{12}) CBC, B_4C(B_{12}) CCC) (Glaser et al., 1953; Thévenot, 1990). This structure suggests potential novel properties of boron carbide at reduced dimensions compared to its bulk phase. However, its poor conductivity limits its energy storage capacity (Avcıoğlu et al., 2023).

Therefore, this study introduces a novel approach by incorporating boron carbide-boron nitride hybrid powder for the first time, aiming to enhance its energy storage potential. The study investigates and discusses the potential of this hybrid powder for energy storage applications.

2. Materials and Methods

The B_4C-BN hybrid powder was synthesized using the sol-gel method as detailed in a previous publication by our research group (Avcıoğlu et al., 2022). The phase composition of the synthesized powders was determined via X-ray diffraction analysis (XRD) using a Bruker D2 Phaser instrument with Cu Kα radiation (λ =1.540 Å, 30 kV, and 10 mA) in the range of 5° to 90°, with a scanning rate of 1°/min. HighScore Plus (version 3.0e-3.0.5) software was employed to analyze the phase ratios based on the XRD data obtained. The morphology of the particles was examined using a scanning electron microscope (SEM), specifically a Jeol JSM-6010LV. Further quantitative elemental analysis of the samples was conducted via SEM-EDX analysis.

The working electrode was fabricated by combining 85 wt.% of the synthesized powder, 10 wt.% of C65 conductive carbon black, and 5 wt.% of poly (vinylidene fluoride) binder dissolved in N,N-dimethyl pyrrolidinone (NMP) solvent. The resulting mixture was applied onto a nickel foam substrate measuring 1 × 1 cm^2. Cyclic voltammetry (CV) measurements were carried out at various scan rates ranging from 5 to 100 mVs^{-1}.

3. Results and Discussion

The XRD analysis results of the synthesized powder without any purification are presented in Figure 1. According to the pattern, the powder contains three crystalline phases: boron carbide (B_4C), hexagonal boron nitride (h-BN), and boron oxide (B_2O_3). The ratios of these phases were determined using HighScore Plus software (version 3.0e-3.0.5). Boron carbide is the predominant phase, comprising 75% of the sample. Hexagonal boron nitride (h-BN) is the second most abundant phase, accounting for 16%. Additionally, a small amount of boron oxide remains as residual, making up 9% of the sample. Boron oxide is known for its high-water solubility, approximately 300 g/L in distilled water at 90 °C. Therefore, the excess boron oxide present in the powder can be easily removed by washing it with hot distilled water. It is notable to mention that any residual carbon-based phases such as amorphous carbon or graphite did not remain in the powder.

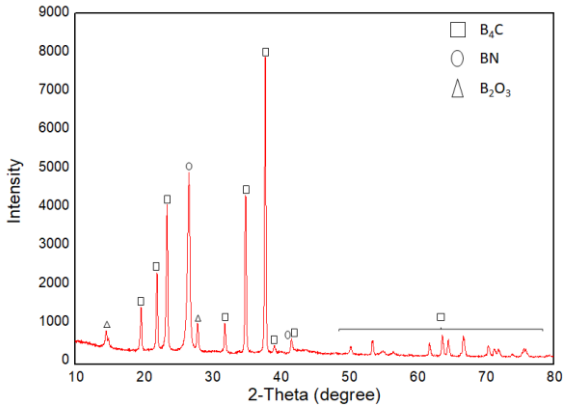

Figure 1. The XRD analysis result of B4C-BN powder.
Şekil 1. B4C-BN tozu için XRD analiz sonuçları.

The SEM images taken from different points of the B_4C-BN hybrid powder are presented in Figure 2. The images revealed that boron carbide particles with plate-like, elongated, and complex-shaped morphology were formed. It was seen that the size of most boron carbide particles is higher than 10 µm. On the other hand, boron nitride formed on the surfaces of boron carbide as clusters of sub-micron-sized particles. The approximate size of the boron nitride particles was observed to be lower than 300 nm.

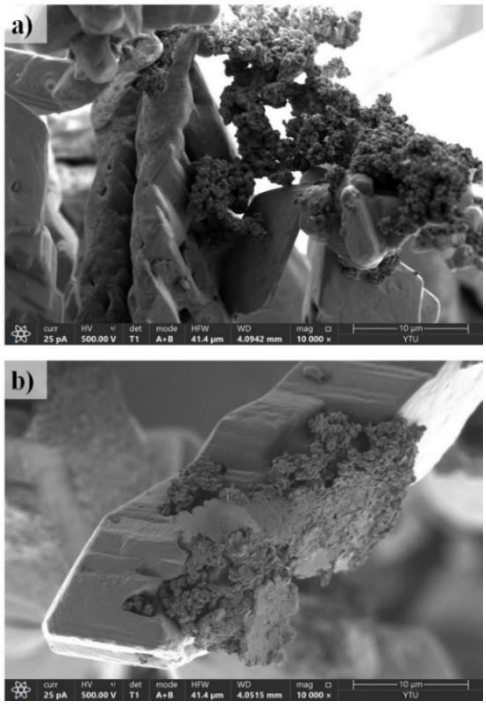

Figure 2. The scanning electron microscopy images of synthesized B_4C-BN hybrid powder.
Şekil 2. Sentezlenmiş B_4C-BN *hybrid tozu için taramalı elektron mikroskobu görüntüleri*

The SEM-EDX mapping results of hybrid powder are presented in Figure 3. Figures 3-a and 3-d reveal that nano-sized particle clusters are nitrogen and boron-rich and seen with pink and red colors in the elemental maps, respectively. The results also show that plate-like and elongated particles are boron carbide Figure 3-a and 3-e.

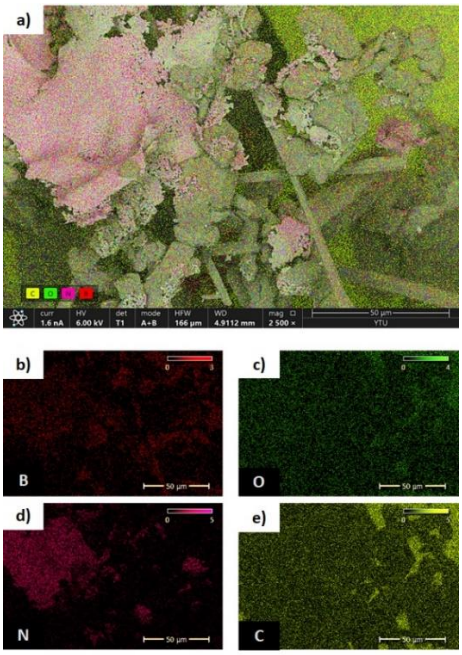

Figure 3. The HR-SEM EDS images of synthesized powder. (a) SEM image, (b) boron map, (c) oxygen map, (d) nitrogen map, and (e) carbon map.
Şekil 3. Sentezlenmiş tozun HR-SEM EDS görüntüleri. (a) SEM görüntüsü, (b) boron haritası, (c) oksijen haritası, (d) azot haritası ve (e) karbon haritası.

To elucidate the charge storage mechanism of the B_4C-BN hybrid powder, cyclic voltammetry (CV) analysis was conducted. The cyclic voltammograms of the electrode were recorded across various scan rates ranging from 5 to 100 mV/s, covering a potential working range of 0-0.4 V in a 6 M KOH aqueous solution, as depicted in Figure 4.

Distinct redox-couple peaks were observed in the CV curves, indicating the pseudocapacitive behavior of the electrode. The consistent shape of the CV curves across different scan rates suggests the stability of the synthesized powders within the chosen electrolyte. Additionally, an increase in the area under the CV curves was noted with higher scan rates.

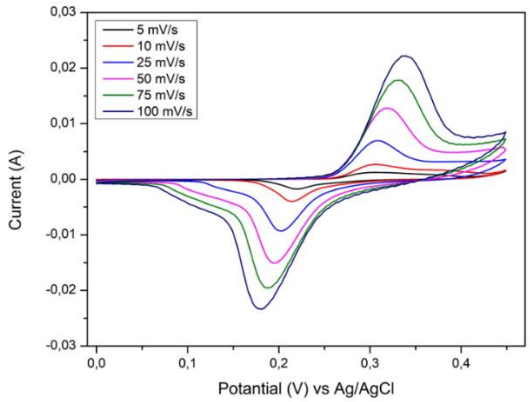

Figure 4. Cyclic voltammetry (CV) curves of the B_4C-BN hybrid powder at different scan rates.
Şekil 4. B_4C-BN hibrit tozu için farklı taranma hızlarında çevrimsel voltametri (CV) eğrileri.

The specific capacitance values of the prepared electrodes were also examined. Equation 1 was applied to derive the specific capacitance values from the CV data obtained at different scan rates. The results obtained from this analysis are illustrated in Figure 5.

$$C_s = \frac{\int_{V1}^{V2} I(V)dV}{mv(V2 - V1)} \quad (1)$$

$\int_{V1}^{V2} \boldsymbol{I(V)dV}$: area under CV curve, $\boldsymbol{m}$: mass of active material (g), $\boldsymbol{v}$: scan rate (V/s).

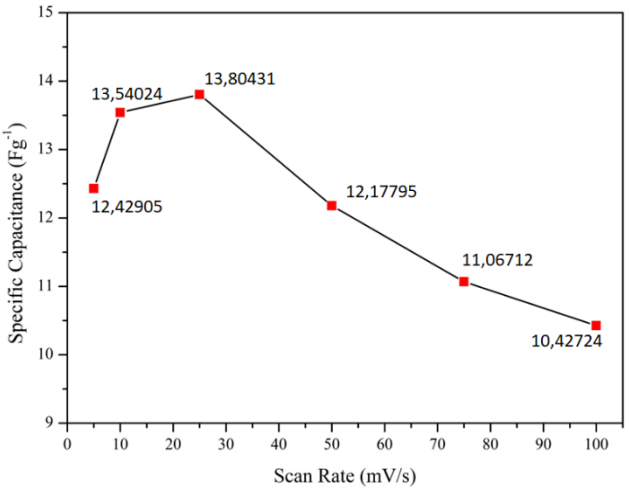

Figure 5. The capacitance values determined as a function of scan rate using CV curves.
Şekil 5. CV eğrileri kullanılarak tarama hızına bağlı olarak belirlenen kapasite değerleri.

As depicted in Figure 5, the highest specific capacitance value of 13.80 F/g was attained at a scan rate of 25 mV/s. Initially, the specific capacitance value shows an increase, followed by a gradual decrease as the scan rate rises. This decrease in specific capacitance value is attributed to the limitation in diffusion caused by the escalating scan rate. At the highest scan rate of 100 mV/s, the lowest specific capacitance value calculated from the CV curves was 10.42 F/g.

4. Conclusion

In conclusion, highly crystalline boron carbide-boron nitride hybrid powder was successfully synthesized via the sol-gel technique at 1500°C heat treatment temperature. The final product contains B_4C, BN, and B_2O_3 phases in ratios of 75-16-9%, respectively. Neither amorphous carbon nor graphite remained in the powder. SEM inspections showed that boron carbide particles formed in various morphologies, and nano-sized boron nitride particle clusters occurred. Electrochemical analysis of B_4C-BN powder-based electrodes revealed the pseudo-capacitive behavior of electrodes. The CV curves were scanned at a rate of 25 mV/s to determine the greatest specific capacitance value, which came out to be 13.8 F/g. The overall results indicate that B_4C-BN hybrid powder has the potential to be an alternative to conventional energy storage materials.

5. Acknowledgements

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6. Conflicts of Interest

The authors declare no conflict of interest.

7. References

Avcıoğlu, S., Ateş, Z. N., Kam, E., Kaya, C., & Kaya, F. (2022). The influence of polyelectrolyte on the synthesis of B4C/BN nanocomposite powders via sol-gel method. *Ceramics International, 48(11)*, 15355-15363. DOI: 10.1016/j.ceramint.2022.02.069.

Avcıoğlu, S., Buldu-Akturk, M., Erdem, E., Kaya, F., & Kaya, C. (2023). Boron carbide as an electrode material: tailoring particle morphology to control capacitive behaviour. *Materials, 16(2)*, 861. DOI: 10.3390/ma16020861.

Avcioglu, S., Kaya, F., & Kaya, C. (2020). Effect of elemental nano boron on the transformation and morphology of boron carbide (B4C) powders synthesized from polymeric precursors. *Ceramics International, 46(11)*, 17938-17950. DOI: 10.1016/j.ceramint.2020.04.104.

Glaser, F. W., Moskowitz, D., & Post, B. (1953). An investigation of boron carbide. *Journal of Applied Physics, 24(6)*, 731-733. DOI: 10.1063/1.1721367.

Liang, C., Tian, F., Li, Z., Feng, Z., Wei, Z., & Li, C. (2003). Preparation and adsorption properties for thiophene of nanostructured W2C on ultrahigh-surface-area carbon materials. *Chemistry of materials, 15(25)*, 4846-4853. DOI: 10.1021/cm034399c.

Sanger, A., Kumar, A., Kumar, A., Jain, P. K., Mishra, Y. K., & Chandra, R. (2016). Silicon carbide nanocauliflowers for symmetric supercapacitor devices. *Industrial & Engineering Chemistry Research, 55(35),* 9452-9458. DOI: 10.1021/acs.iecr.6b02243.

Thevenot, F. (1990). Boron carbide—a comprehensive review. *Journal of the European Ceramic society, 6(4)*, 205-225. DOI: 10.1016/0955-2219(90)90048-K.