EFFECT OF ORGANIC LINKERS AND GRAPHENE LOADING ON TERNARY METAL ORGANIC FRAMEWORK COMPOSITE FOR ASYMMETRIC SUPERCAPACITOR APPLICATION

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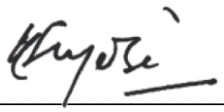

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ABSTRAK

Superkapasitor (SCs) ialah peranti simpanan tenaga yang mempunyai ketumpatan kuasa (P_D) yang tinggi, keupayaan pengecasan pantas, dan jangka hayat yang panjang. Secara asasnya, ia terdiri daripada dua jenis bergantung kepada mekanisma simpanan cas dalam superkapasitor iaitu kapasitor elektrik dua lapisan (EDLCs) dan pseudokapasitor (PCs). Terdapat jenis yang ketiga, dipanggil hibrid bateri-superkapasitor, menggabungkan mekanisma EDLC dan PC. Simpanan cas bagi EDLCs adalah melalui pengumpulan cas elektrik berbalik pada antara muka elektrod-elektrolit dan bersifat tidak faraday. PC menyimpan cas secara tindak balas faraday dalam beberapa lapisan elektrod. Fabrikasi SC menggunakan satu elektrod PC dan satu lagi elektrod EDLC atau dikenali sebagai superkapasitor asimetri (ASCs) menggabungkan kesan berguna kedua-duanya. Kajian ini bermatlamat untuk mensintesis dan mencirikan bahan elektrod PC iaitu $Co(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2$, dan $Ni(NO_3)_2 \cdot 6H_2O$ untuk mencipta satu kerangka organik logam baharu bersama penghubung organik yang berlainan iaitu asid tereftalik, trimellitik, dan piromellitik. Seterusnya, komposit ini digabungkan bersama grafin terdop-N iaitu bahan EDLC untuk superkapasitor asimetri (ASCs) untuk meningkatkan sifat kapasiti sebagai elektrod SC. Bahan-bahan dicirikan menggunakan mikroskop elektron pengimbasan pelepasan medan (FESEM), pembelauan sinar-X (XRD), spektroskopi transformasian Fourier inframerah (FTIR), kajian penjerapan gas, dan analisis termogravimetri (TGA). FESEM-EDX menunjukkan kehadiran unsur-unsur yang sepadan iaitu kobalt (Co), tembaga (Cu), dan nikel (Ni) dalam rangka kerja. XRD menunjukkan struktur kristal yang terdapat dalam sampel Co/Cu/Ni kecuali Co/Cu/Ni-tri. Co/Cu/Ni-tetra menunjukkan struktur kristal. FTIR menunjukkan interaksi kumpulan fungsi yang terdapat pada MOF dan pemaut organik. Ia terdiri daripada O-H, C-H, dan C=C regangan dan lenturan. Bagi unsur-unsur, Cu-O, Co-O, dan Ni-O yang hadir di MOF. Analisis BET menunjukkan Co/Cu/Ni-tetra mempunyai lengkung IV jenis biasa dan kehadiran gabungan mikroliang dan mesoliang di MOF. TGA menunjukkan puncak degradasi dalam sampel MOF dengan suhu yang sepadan, dan Co/Cu/Ni-tetra menjalani empat peringkat penurunan berat badan dalam julat suhu 25–900 °C dengan sisa akhir pada 36%. Sifat elektrokimia bahan dinilai menggunakan voltammetri berkitar (CV), kitaran cas-discas galvanostatik (CDC), dan spektroskopi impedans elektrokimia (EIS). MOF ternari yang disediakan menggunakan pemaut asid piromellitik dan diubah suai dengan 3 wt. % NG (Co/Cu/Ni-tetra/NG-3%) menunjukkan prestasi keseluruhan terbaik dengan kapasitans tertentu 1,136 Fg^{-1} pada 1 Ag^{-1}. ASC telah direka menggunakan Co/Cu/Ni-tetra/NG-3% sebagai elektrod positif dan karbon diaktifkan (AC) sebagai elektrod negatif. Co/Cu/Ni-tetra/NG-3%//AC dalam 6 M KOH memberikan prestasi tinggi E_D tetapi P_D yang lebih rendah, sebanyak 30.4 kg^{-1} dan 850 W kg^{-1}, manakala dalam PVP-KOH gel elektrolit polimer, ASC memberikan E_D 21.6 Wh kg^{-1} pada P_D 950 W kg^{-1}. Ujian kestabilan pada Co/Cu/Ni-tetra/NG-3%//AC jauh lebih baik dalam 6 M KOH dengan pengekalan ~80%, manakala ~60% dalam PVP-KOH selepas 1,000 kitaran kerana pergerakan ion elektrolit yang lebih baik dalam sel.

ABSTRACT

Supercapacitors (SCs) are energy storage devices with high power density (P_D), medium energy density (E_D), fast recharge capability, and long cycle life. There are fundamentally two types of energy storage mechanisms in supercapacitors which are electrical double-layer capacitors (EDLCs) and pseudocapacitors (PCs). A third type, called battery – supercapacitor hybrid (BSH), combines the EDLC and PC mechanism. The EDLC stores charge by the reverse accumulation of electric charges at an electrode-electrolyte interface and are non-faradaic, whereas the PC stores charge through a faradaic reaction within a few layers of the electrode. Asymmetric supercapacitors (ASCs) are fabricated using one of its electrodes of PC materials and the other one is EDLC material, combining their beneficial effects. This research pursues the synthesis and characterisation of PC material precursors, which are $Co(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2$, and $Ni(NO_3)_2 \cdot 6H_2O$ to form a ternary metal-organic framework (MOF) with different organic linkers, which are terephthalic, trimellitic, and pyromellitic acids via hydrothermal method. The MOF was further modified with N-doped graphene (NG) to enhance the capacitive properties of the SC electrode. The materials were characterised by field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, gas adsorption studies, and thermogravimetric analysis (TGA). FESEM-EDX showed the presence of the corresponding metal precursor elements in the frameworks (i.e., cobalt (Co), copper (Cu), and nickel (Ni)). The XRD analysis showed the crystalline structures of the Co/Cu/Ni-MOF samples, except for Co/Cu/Ni-tri. The FTIR results showed the interaction of the functional groups present in the MOF, including O-H, C-H, C=C, Cu-O, Co-O, and Ni-O vibrational bands. According to the Brunauer-Emmett-Teller (BET) analysis, Co/Cu/Ni-tetra possessed a typical type IV curve, displaying a combination of micropores and mesopores in the MOF. The TGA demonstrated the degradation peaks in the MOF samples with the corresponding temperature, and Co/Cu/Ni-tetra experienced four stages of weight loss in the temperature range of 25–900 °C with a final residue of 36%. The electrochemical properties of the materials were evaluated using cyclic voltammetry (CV), galvanostatic charge-discharge cycling (CDC), and electrochemical impedance spectroscopy (EIS). The ternary MOF prepared using pyromellitic acid as a linker and modified with 3 wt% NG (Co/Cu/Ni-tetra/NG-3%) demonstrated the best electrochemical performance with a specific capacitance (C_S) of 1,136 F g^{-1} at 1 A g^{-1} in 6 M KOH electrolyte. The ASCs were fabricated using Co/Cu/Ni-tetra/NG-3% as a positive electrode and activated carbon (AC) as a negative electrode. The Co/Cu/Ni-tetra/NG-3%//AC in 6 M KOH gave a high E_D of 30.4 Wh kg^{-1} at P_D 850 W kg^{-1}, whereas in PVP-KOH gel polymer electrolyte, the ASC recorded E_D of 21.6 Wh kg^{-1} at P_D of 950 W kg^{-1}. The ASC stability was much better in 6 M KOH with ~80% retention, whereas ~60% retention was recorded in PVP-KOH after 1,000 cycles due to the better electrolyte ion movement in the cell.

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