

**SUPERCAPACITORS BASED ON CARBON NANOTUBES AND
HYBRID POLYMER ELECTROLYTES**

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ABSTRAK

Kepentingan superkapasitor tidak boleh diberi lebih penekanan terutamanya didalam era pencarian untuk penambahbaikan peranti simpanan tenaga yang fleksibel secara mekanikal, lebih ringan, dan lebih kompak untuk signifikan aplikasi; daripada tenaga yang boleh diterap dalam pakaian sehingga kepada aplikasi angkasa yang mana kos berdasarkan berat dan isipadu sangat tinggi. Superkapasitor sangat menarik untuk alat elektronik mudah alih juga aplikasi disebabkan oleh ketahanan dan kuasa spesifik yang tinggi. Penyelidikan ini berfokus pada fabrikasi sel superkapasitor yang menggunakan nanotub karbon sebagai bahan utama elektrod aktif dan elektrolit hibrid sebagai pemisah. 90% daripada setiap karbon komersial digunakan iaitu *Carboxyl*, *Hydroxyl* dan *Normal CNTs* serta 10 % *Polyvinylidene fluoride (PVDF)* dan *Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP)* sebagai pengikat telah dipilih untuk menghasilkan filem elektrod. Dalam pada itu, dua jenis elektrolit polimer yang berbeza - *Pure Solid Polymer Electrolyte (PSPE)* dan *Hybrid Solid Polymer Electrolytes (HSPE)* (disorap ke dalam kertas turas selulosa) – disediakan daripada campuran *polyvinyl alcohol (PVA)* dan *orthophosphoric acid (H₃PO₄)* dengan nisbah yang berbeza dari 0 wt.% sehingga 70 wt.%. Ujian kekonduksian dijalankan pada suhu bilik menunjukkan elektrolit *HSPE* memberikan kekonduksian yang tertinggi iaitu $1.67 \times 10^{-3} \text{ Scm}^{-1}$ berbanding *PSPE* ($2.56 \times 10^{-3} \text{ Scm}^{-1}$). Berdasarkan keputusan ini, menyedari potensi *HSPE* melebihi *PSPE*, sel superkapasitor difabrikasi dari 50, 60 dan 70 wt.% phosphoric acid dalam campuran *PVA/H₃PO₄/selulosa* (cth. H50, H60 and H70). Kesemua sel superkapasitor diuji tahap kitaran dan cas – discas (*CD*). Daripada sembilan sel yang dihasilkan (tiga dari setiap sampel *CNTs*), *C90H70* (cth. *Cell - C (C90PVdF-HFP10 |H70) C90PVdF-HFP10*)) menunjukkan kapasitans yang tinggi iaitu 313 Fg^{-1} bila dihitung menggunakan *Cyclic Voltammetry (CV)* berjulat $0.0 - 1 \text{ V}$. Bagaimanapun, dalam ujian *CD*, kapasitans efektif, ketumpatan tenaga dan kuasa yang diperoleh masing-masing ialah 153 Fg^{-1} , 76.50 Whg^{-1} dan 1.00 Wg^{-1} , dan purata kecekapan sehingga 93.8 % dengan lebih 5000 keupayaan kitaran. Ujian lain yang juga penting dilakukan ke atas kedua-dua sampel elektrod dan elektrolit iaitu *Thermogravimetric Analysis (TGA)*, *Field Emission Scanning Electron Microscope (FESEM)*, *X-Ray Diffraction (XRD)*.

ABSTRACT

The importance of supercapacitors cannot be over emphasized, especially in this current era of search for an improved energy storage device that is mechanically flexible, more lightweight, and more compact for use in a significant number of applications; from wearable energy that could be incorporated into garments, to space applications where the cost by weight and volume is huge. Supercapacitors are very attractive for portable electronics as well as automotive applications due to their high specific power and durability. This research focuses on the fabrication of supercapacitor cells using carbon nanotube as the main active electrode material and hybrid polymer electrolyte as the separator. 90 % of each of the following commercially prepared carbon nanotubes namely; Carboxyl, Hydroxyl and the Normal CNTs and 10 % of polyvinylidene fluoride (PVDF) and Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) as a binder have been selected for the electrode film. On the other hand, two different types of aqueous polymer electrolytes – Pure Solid Polymer Electrolyte (PSPE) and Hybrid Solid Polymer Electrolytes (HSPE) (incorporated with cellulose filter paper) – were prepared from the solution of polyvinyl alcohol (PVA) and orthophosphoric acid (H_3PO_4) in different percentage ratios from 0 wt. % to 70 with. %. Conductivity studies conducted at room temperature shows that the electrolyte made from HSPE delivered the highest conductivity of $1.67 \times 10^{-3} \text{ Scm}^{-1}$ as against PSPE ($2.56 \times 10^{-3} \text{ Scm}^{-1}$). Based on these results, and having noticed the potentials that HSPE had over PSPE, Supercapacitor cells were fabricated from 50, 60 and 70 wt.% of phosphoric acid in PVA/ H_3PO_4 /cellulose blends (i.e. H50, H60 and H70). All the supercapacitor cells have been tested for their cyclic behaviors and galvanostatic charge-discharge (CD). Of the Nine successfully fabricated cells (three from each sample of CNTs), C90H70 (i.e. Cell – C (C90PVdF-HFP10 |H70| C90PVdF-HFP10)) delivered the highest capacitance of 313 Fg^{-1} when calculated using cyclic voltammetry within the electrochemical voltage window of 0.0 – 1 V. However, when measured by galvanostatic CD, its effective capacitance, energy and power densities obtained are 153 Fg^{-1} , 76.50 Whg^{-1} and 1.00 Wg^{-1} respectively, and attained the overall columbic efficiency of 93.8 % with more than 5000 cycleability. Other important tests conducted on both samples of electrode and electrolytes are Thermogravimetric Analysis (TGA), Field Emission Scanning Electron Microscope (FESEM), X-Ray Diffraction (XRD).

ملخص

أهمية المكثفات الفائقة لا يمكن التغاضي عنها، خاصة في هذا العصر الحالي من البحث لتحسين وسيلة تخزين الطاقة المرنة ميكانيكياً، أكثر خفة في الوزن وأكثر احكاماً للاستخدام في عدد كبير من التطبيقات، من الطاقة القابلة للارتداء التي بالامكان دمجها بالملابس، الى تطبيقات الفضاء التي تكلفتها من حيث الوزن والحجم ضخمة. المكثفات الفائقة مناسبة جداً للإلكترونيات المحمولة وكذلك تطبيقات السيارات بسبب قوتها العالية والدقيقة ومتانتها. هذا البحث يركز على تصنيع خلايا المكثفات الفائقة باستخدام أنابيب الكربون الدقيقة على أنها المادة الرئيسية النشطة للقطب والبوليمر المهجن الكهربائي كفاصل. 90% من أنابيب الكربون الدقيقة المحضرة التالية المسماة، كربوكسيل، هيدروكسيل، و CNTs العادي و 10% من بولي فينيلدين (PVDF) و بولي (فينيلدين فلورايد-كو-هيكسافلوروبروفيلين) (PVDF-HFP) كتوتيق تم اختيارها لفلم القطب. على الجانب الأخر، نوعين مختلفين من البوليمر المائي الكهربائي - البوليمر الكهربائي النقي الصلب (PSPE) و البوليمر الكهربائي الصلب المهجن (HSPE) (أدرجت مع ورقة السيليلوز للتصفية) - حضرو من محلول من كحول متعدد الفينيل (PVA) وحمض الأورثوفسفوريك (H_3PO_4) بتراكيز مختلفة تبدأ من 0 إلى 70%. دراسات توصيل أجريت في درجة حرارة الغرفة وضحت ان المنحل الكهربائي المصنوع من HSPE يعطي أعلى توصيل 10×1.67 ضد 10×2.56 PSPE اعتماداً على هذه النتائج، و ملاحظة امكانية ان HSPE له قدرة أعلى من PSPE، خلايا المكثفات الفائقة عدلت من 50، 60 و 70% من حمض متعدد الفسفوريك في مزيج من PVA/ H_3PO_4 /Cellulose (i.e. H50, H60 and H70). كل خلايا المكثفات الفائقة اختبرت على قدرتها الحلقية و قلوفونوستيك شحن-تفريغ الشحن (CD). من تسع خلايا معدلة ناجحة (ثلاثة من كل عينة من CNTs)، (C90PVdF-HFP10 | H70 | C90PVdF-HFP10) أعطت أعلى سعة وهي 313 Fg^{-1} عند حسابها باستخدام مقياس فولتامتري الحلقي عند الجهد الكهروكيميائي 0.0 - 1 فولت. على الجانب الأخر، عند القياس باستخدام قلوفونوستيك CD، سعتها فعالة، طاقة وقوة الكثافة المتحصلة هي 153 Fg^{-1} ، 76.50 Whg^{-1} و 1.00 Wg^{-1} على التوالي، و حققت من كل كفاءة الكولومبيك 93.80% مع أكثر من 5000 سيكلابيليقي. اختبارات اخرى مهمة أجريت على العينتين الاثنتين القطب الكهربائي والشوارد الكهربائية هي

تحليل تيرموغرافيميتريك (TGA)، مجهر حقل انبعاث الماسح الضوئي الالكتروني (FESEM)، الأشعة السينية
الحيادية (XRD).

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ABBREVIATIONS

AC	Activated Carbon
BET	Brunauer–Emmett–Teller
CB	Carbon Black
CD	Charge-Discharge
CNTs	Carbon Nanotubes
CPCMWCNT	Commercially Prepared Carboxyl Multiwalled Carbon Nanotubes
CPEs	Composite Polymer Electrolytes
CPHMWCNT	Commercially Prepared Hydroxyl Multiwalled Carbon Nanotubes
CPNMWCNT	Commercially Prepared Normal Multiwalled Carbon Nanotubes
CV	Cyclic Voltammetry
CVD	Chemical Vapor Deposition
DI	Deionized
ECs	Electrochemical/Electric Capacitors
EDLC	Electric/Electrochemical Double layer Capacitor
FESEM	Field Emission Scanning Electron Microscope
GPEs	Gel Polymer Electrolytes
H ₂ SO ₄	Sulfuric Acid
H ₃ PO ₄	Orthophosphoric Acid
KCL	Potassium Chloride
KOH	Potassium Hydroxide
MCCD	Multichannel Charge-Discharge
MWCNTs	Multiwalled Carbon Nanotubes
Na ₂ SO ₄	Sodium Sulfate
P(VdF-HFP)	Poly(vinylidene fluoride- <i>co</i> -hexafluoropropylene)
PAS	Polyacenic Semiconductor
PE	Polyethylene
PEs	Polyelectrolytes
PP	Polypropylene
PPy	Polypyrrole
PTFE	Polytetra fluoroethylene
PVA	Polyvinyl Alcohol
PVDC	Poly(vinylidene chloride)
PVDF	Polyvinylidene Fluoride
SEM	Scanning Electron Microscope

SFPE
SPEs
SSPE
SWCNTs
XRD

Solvent Free Polymer Electrolytes
Solid Polymer Electrolytes
Solvent Swollen Polymer Electrolytes
Singlewalled Carbon Nanotubes
X-Ray Diffraction

