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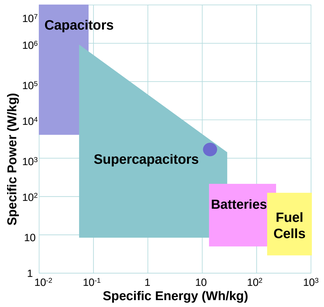
Introduction

❖ Electrochemical double layer capacitors (EDLCs) are promising for energy storage that requires high-power & high-energy density.

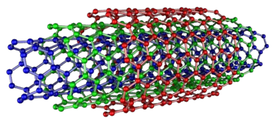
❖ EDLC performance is correlated with the electrode surface area.

❖ The development of nanomaterials and nanostructured electrodes is expected to provide enhancements in key properties.

❖ **Carbon nanotubes (CNTs)** have a unique set of properties such as high electrical conductivity, electrochemical, mechanical and chemical stability, high surface area and low mass density.

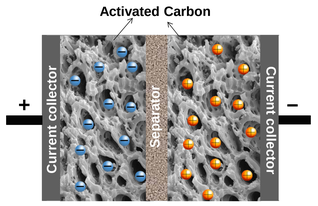


❖ **Vertically aligned carbon nanotubes (VACNTs)** are considered due to their facile synthesis and the ability to control the ion-accessible surface.



❖ Continuous methods to synthesize VACNTs at low costs are needed for commercially viable EDLCs.

EDLC supercapacitor



Objective

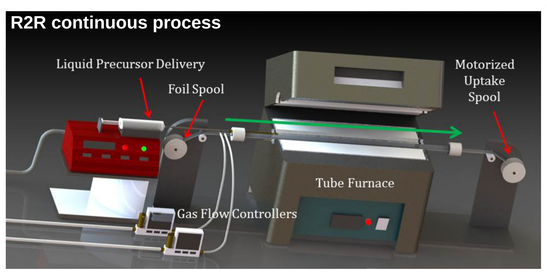
❖ Develop a commercially feasible low temperature continuous process for VACNTs growth on inexpensive current collectors for EDLC electrodes.

Electrodes preparation

❖ Current VACNT production methods: electric arc discharge, laser ablation and chemical vapor deposition (CVD).

❖ CVD is a practical and reliable method for synthesizing VACNT forests with the ability to control CNT tube diameter, number of walls and dopant ratio.

❖ 3 types of electrodes were investigated: VACNTs grown using a stationary CVD process (sCVD) and a continuous roll-to-roll process (R2R), and buckypaper (BP) comprising randomly-oriented commercial CNTs.



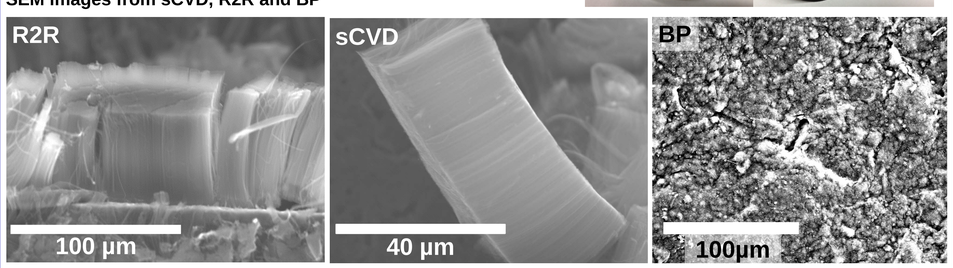
❖ An R2R process was developed to synthesize VACNTs directly on motor-drawn Al foil.

❖ Floating catalyst ferrocene-xylene method was used in the presence of Ar, C_2H_2 and H_2 gases.

❖ Low temperature allows for deposition on low-cost substrates

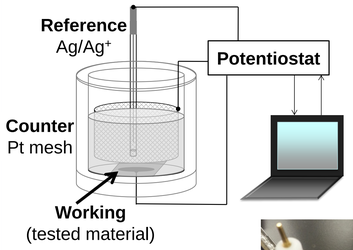
Al foil rolls before and after CNT growth →

SEM images from sCVD, R2R and BP

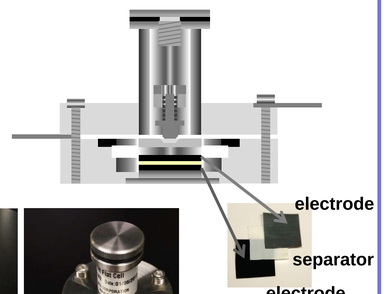


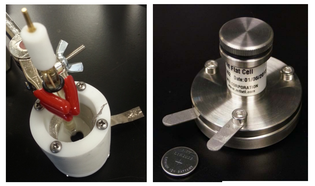
Electrochemical Characterization

3-electrode cell



2-electrode cell

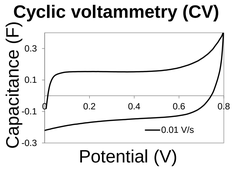




Energy and power density

$$W = \frac{1}{2}CV^2 \qquad P = \frac{W}{t}$$

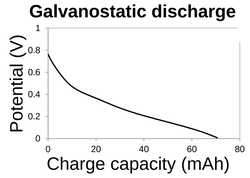
Cyclic voltammetry (CV)



❖ Capacitance: ability of a body to store charge.

$$C_{sp} = \frac{\int IdV}{2\Delta V m v}$$

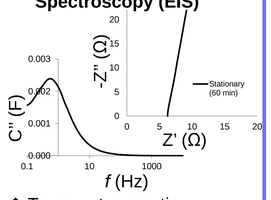
Galvanostatic discharge



❖ Charge capacity: electric charge a device can deliver at a voltage.

❖ Cycling stability

E-chem Impedance Spectroscopy (EIS)



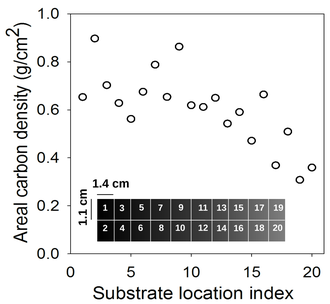
❖ Transport properties

❖ Relaxation time t = $1/f_{peak}$ Time to discharge to 50%.

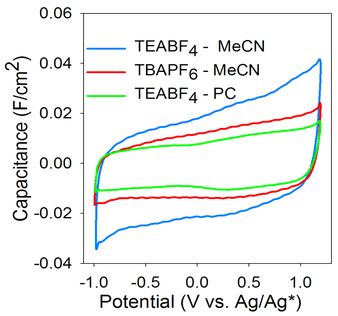
Results

Characterization of sCVD-growth CNTs
3-electrode cell

Spatial distribution of VACNT areal density



CV profiles in 3 different electrolytes



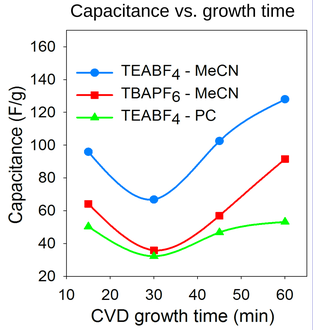
❖ The amount of CNTs grown with CVD depends on the runtime and substrate location relative to the injection nozzle.

❖ Nearly uniform growth areas: locations 1-8 with CNT height of ~50 mm after 1 h of growth.

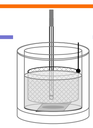
❖ From CV profiles: the highest specific capacitance measured was 135 F/g in $TEABF_4$-MeCN.

❖ The increasing specific capacitance with growth time arises from an increase in CNT areal density.

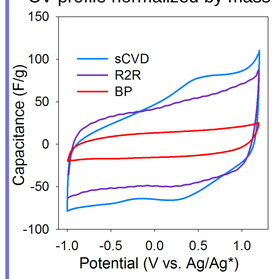
Capacitance vs. growth time



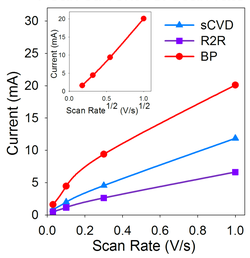
Comparison of sCVD, R2R and BP
3-electrode cell



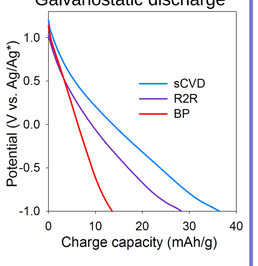
CV profile normalized by mass



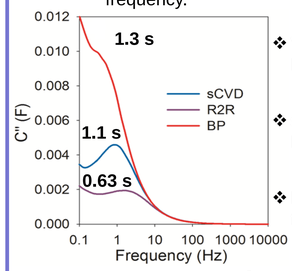
Peak current vs. scan rate



Galvanostatic discharge



Imaginary capacitance vs. frequency.



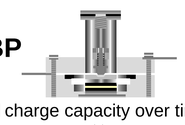
❖ R2R: improved capacitance (51 F/g) vs. BP (13.6 F/g).

❖ VACNT did not show any significant ion-diffusion limitations. BP exhibited a sub-linear current dependence on scan rate.

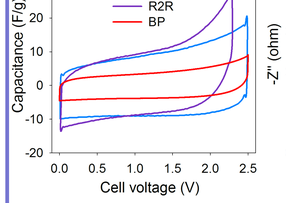
❖ sCVD had the highest charge capacity (36.7 mAh/g) vs. R2R and BP with 24.8 and 13.6 mAh/g.

❖ R2R exhibited faster discharge times with a lower relaxation time constant (630 ms vs 1.1 s).

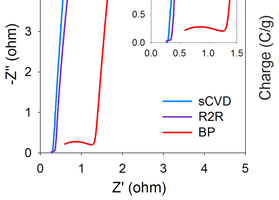
Comparison of sCVD, R2R and BP
2-electrode cell



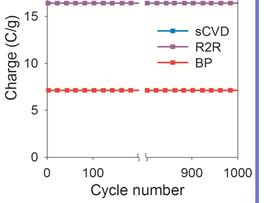
CV normalized by mass



Nyquist plot



Total charge capacity over time



❖ sCVD and R2R show similar EDLC performance with higher specific capacitance than BP.

❖ The Nyquist plot for EDLC cells shows significantly lower internal resistance for sCVD and R2R compared to BP electrodes.

❖ The performance of all the EDLC cells was stable for over a thousand cycles without any degradation.

Summary

❖ A scalable process for the production of CNTs is needed, to achieve commercially viable EDLCs from this material.

❖ We have developed a relatively low cost R2R process to synthesize VACNT electrodes directly on Al foils at a low temperature (600 °C) using a ferrocene-xylene solution-based method.

❖ R2R EDLC exhibited the highest performance in terms of capacitance, energy density and power density.

❖ All devices showed excellent cycle stability.

Carbon (type)	Capacitance (F/g)	Power (W/kg)	Energy (Wh/kg)
R2R	9.6	1270	11.4
sCVD	9.1	1210	10.2
BP	4	650	4.9