Research Article

Supercapacitor by using different size of Activated Carbon from Palm Oil Kernel (PKS) as EDLC Electrode

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***Abstract**: The large oil palm plantation in Malaysia is located in Sabah which is around 700,000 acres of land that produces around 0.7 million tons of agricultural waste. The conversion of agriculture waste to activated carbon (AC) solves the disposal problem in the agricultural industry. The AC plays an important role as an electrode in supercapacitor due to its characteristics such as high porosity and good conductivity. The performance of supercapacitor electrodes was study by using different sizes of AC. The AC from oil palm kernel shell (PKS) was produced by using the low cost of production with a simple modification in a conventional method. The PKS carbonizes in a furnace at 390 oC for 1 hour. It soaks in KOH for chemical activation. The sample is rushed by using agate mortar to get two different sizes which is fine and coarse. The AC is then mixed for the preparation of the electrode labelled as (Sample 1, Sample 2 & Sample 3). Then, the electrode is assembled with filter paper as separator and 1.0 M KOH as electrolyte. The supercapacitor electrode is connected to the circuit to observe the potential of charge-discharge. The result of capacitance for Sample 1 is 26.3mF, specific capacitance 21.58mF/g and energy density 17.22Wh/kg while the Sample 2 of activated carbon is 2672.38mF, 1113.49 mF/g and energy density 52.384Wh/kg and Sample 3 is 2952.5mF, specific capacitance 1230.16mF/g and energy density 226.34Wh/kg. As conclusion, a high-performance capacitor is achieved by using a mixed size of PKS as active material in electrode. Therefore, PKS has large market potential due to the low-cost AC production but promises high performance in Supercapacitor Application.*

Keywords: PKS; Activated Carbon; EDLC; Supercapacitor; Capacitance.

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1. INTRODUCTION

Indonesia and Malaysia are the world's largest producers of agricultural commodities such as palm oil. Nearly 85% of the palm oil consumed worldwide is produced in both nations (Papilo et al., 2022). However, much agricultural waste from oil palm facilities can contribute to environmental pollution. Therefore, abundant agricultural wastes should be used as feedstock for activated carbon (AC) production for supercapacitors. Supercapacitors, also called Electrical double-layer capacitors (EDLCs), use activated carbon as a starting material source (Aziz et al., 2017). ACs are obtained from coal, biomass products, polymers, etc. Nowadays, there is a great interest in finding low-cost and effective alternatives to the existing commercial AC. Research into effective and low-cost AC can contribute to environmental sustainability and provide benefits for future commercial applications. The cost of AC produced from biological resources is incredibly low compared to the cost of commercial AC. Therefore, due importance must be given to bioresources in the synthesis of AC. AC has a high specific surface area, chemical stability, good conductivity, and charge storage capability at the electrode/electrolyte interface and is inexpensive compared to other materials used in electrode fabrication. The selection of raw material is generally based on seven key factors: high carbon content, low organic matter content for low ash results, high density, high volatile matter content, abundance so that the raw material is always very cheap, potential degree of activation, low degradation rate during storage, and potential to produce activated carbon with high percent yield (Chuayboon & Abanades, 2022; Sutarsis & Chang, 2021).

Electric vehicle technology is rapidly advancing, necessitating the use of batteries and supercapacitors as energy storage devices with high energy density and power capacity for use in environmentally friendly automobiles (Yamagata et al., 2014). A hybrid system for energy storage in automobiles combines the advantages of high battery energy density benefits of batteries with the high supercapacitor power density of supercapacitors in a single device unit (Sung et al., 2015). EDLCs are among the most widely used commercial SCs because of their advantages such as longer life, quicker charging times, lighter and safer design, which is without a charging current limit, and effortless to maintain operation. EDLCs with larger particle sizes demonstrated reduced capacitance retention as the discharge rate rose (Portet et al., 2008). The small particle fraction on the electrode and the processing time in ball milling to produce submicron particles affect the efficiency of the EDLC performance (Rennie et al., 2016). The charge storage capabilities of the electrochemically activated carbon material are enhanced in this study by the fabrication of an asymmetric EDLC layer with fine and coarse (between large and small), ACs particles.

2. METHOD & MATERIAL

2.1 Equipments

2.1.1 Furnace, model: CWF 11/23, supplier: HI-CHEM SUPPLIERS SDN BHD

2.1.2 Drying oven, model: MEMMERT, serial no : B219.0761

2.2 Chemicals

2.2.1 Potassium hydroxide (1.0 M KOH)

2.2.2 Hydrochloric acid (1.0 M HCL)

2.2.3 Acetone

2.3 Material

Oil palm kernel shells (PKS) for the activated carbon were collected from different location in Kota Kinabalu, Sabah. The materials were sun-dried as shown in Figure 1. The shells were initially dried for 4 days in the sun, turning them occasionally to drain moisture. Then it was cleaned and chemically activated (Adekola et al. 2005).

Figure 1. Drying PKS collected

2.4 Sample preparation

Dust and other contaminants were removed from the PKS by repeatedly cleaning them with distilled water. It was subjected to pre-treatment procedures where it was crushed in small size and wrapped with four layers of aluminium foil sheets to keep oxygen out of the sample. After that, it required in the furnace, physical steam activation took place after an hour of low carbonization at a temperature of 390^{0}C as shown in Figure 2. Then it was immersed in Potassium hydroxide (1.0 M KOH) to activate the chemical reaction. Following pre-treatment, PKS are decreased in size and dried to a black colour. The sample needs to be crushed into two different sizes, fine and coarse, using an agate mortar.

Figure 2. PKS wrapped by aluminium foil after physical steam in furnace

2.5 Preparation of activated carbon

In order to prepare the electrode, the sample was quickly ground into powder. The mixtures contain PKS powder as activated carbon (AC), casein, white glue, distilled water, and acetone as ratio shown as table below:

Table 1: Components of mixtures

Activated carbon	Casein	White glue	Distilled water	Acetone
0.4g	0.4g	0.2g	3.4ml	0.7ml

The components were stirred by a magnetic stirrer for 30 minutes to get a homogeneous mixture before coating the slurry on aluminium foil. The glass rod was used to apply the AC on the aluminium foil and dried in an oven at 70^0C overnight as shown in Figure 3.

Figure 3. Mixtures coating on aluminium foil using glass rod

2.6 Preparation of electrode plate

After getting the activated carbon, a sheet of aluminium foil was used to saturate the carbon electrode and create the positive and negative electrodes. The electrode was divided by three samples.

Table 2: List of EDLCs Sample

Type of Electrode	Symmetry		Asymmetry
Name of Sample	Sample 1	Sample 2	Sample 3
Size of AC-PKS	Anode – Fine Cathode – Fine	Anode – Course Cathode - Course	Anode -fine Cathode- Course

As shown in Figure 4, the electrode of Sample 3 which is cathode as coarse electrode and anode as a fine electrode were placed on glass as substrate to hold the electrode in placed.

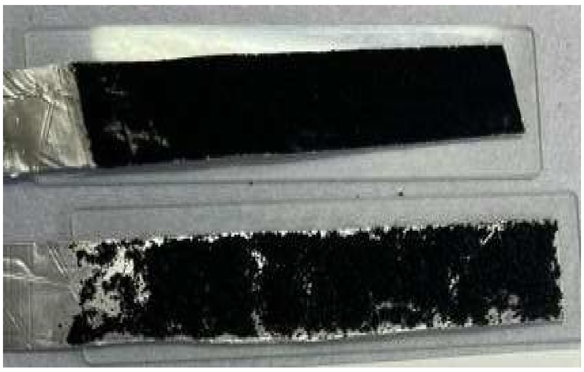

Figure 4. Top is fine electrode and bottom is coarse electrode

1M KOH electrolyte was prepared and sandwiched as well as filter paper as separator in between the electrodes as shown in Figure 5. The AC electrode, which should be facing the separator, was placed towards the bottom. The samples were pressed to make sure the electrodes are in close proximity to one another.

Figure 5. Sandwiched activated carbon

2.7 Preparation of Electric Double Layer Capacitor (EDLC) Supercapacitor

After obtain the sandwiched activated carbon as known as EDLC, the cathode and anode electrodes were identified as positive and negative point, respectively. These points were connected by alligator clips to the charge-discharge circuit. The circuit was supplied by 4V power supply, 1.5 kΩ resistor and voltmeter to monitor the performance of EDLC as shown in Figure 6.

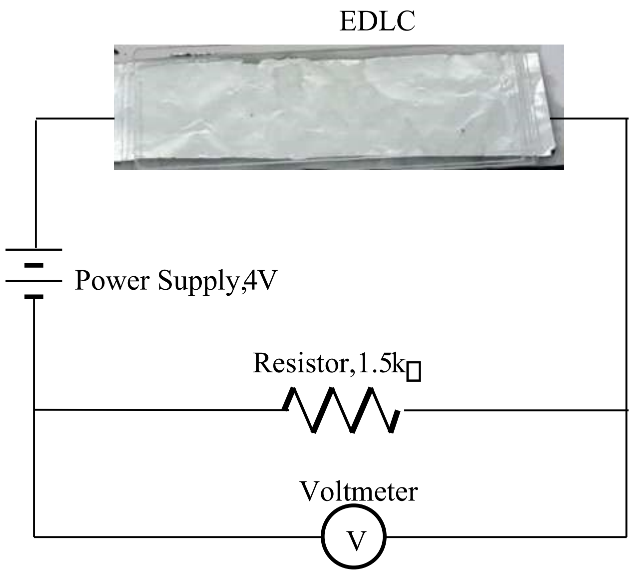

Figure 6. Schematic diagram charge-discharge circuit

3. FINDINGS

In complete cell of supercapacitor, its important parameters to determine the electrochemical properties such as capacitance (F), specific capacitance (F/g) and energy density (Wh/kg). The data collected from charge discharge was calculated to determine the capacitance, C by using equation below.

C= $2 \underline{\qquad\qquad} x\ (DischRxarge\ ((V\ Ftime)2-()VxI()V2average)\ )2$ (F)

where R= Resistance, V_F = maximum working voltage and V_I= minimum working voltage.

Next, the specific capacitance of 2 electrode cell was calculated as follow:

$$\text{Specific Capacitance} = \frac{2C}{m}\ \text{(F/g)}$$

Where m= mass of active material in electrode (g).

The specific energy density of supercapacitor can be calculated by using equation below as quantity per mass or per unit volume.

$$\text{Energy Density, E} = \frac{1}{2} x\ Specific\ Capacitance\ x((V_F)^2 - (V_I)^2)\ \text{(Wh/kg)}$$

3.1 Working Voltage, Discharge Time and Cycle Life.

Three samples are run by charged with 4V power supply to identify the performance for the initial cycle of EDLCs, the data obtained as recorded in Table 3.

From Table 3, it shown the sample 2 (course) obtain lowest working voltage (< 1V) and highest discharge time, meanwhile sample 1 (fine) has mid working voltage (>2V) and lowest charging time. The combination electrode (asymmetric), sample 3 manage to improve the performance of sample 1 by increased the value of working voltage and discharge time. The sample 1 and sample 2 have short cycle life (less than 6 cycle) which is after 6 cycle the capacitance was loss more the 70% for both samples, while the sample 3 can performance more than 20 cycle life with increasing capacitive by increasing the number of cycles.

Table 3: The data of first three cycle for the samples

Name of Sample/Cycle	Sample 1		Sample 2		Sample 3	
	Working Voltage (V)	Discharge time (s)	Working Voltage (V)	Discharge time (s)	Working Voltage (V)	Discharge time (s)
1	2.38	13. 06	0.58	600	3.28	20
2	2.39	12.85	0.55	538	3.45	38
3	2.39	12.53	0.52	245	3.5	20

3.2.2 Charge Discharge Graph of Samples.

The charge discharge graph was plotted to observe the performance of EDLCs for three samples. The symmetric triangle graph was identified as supercapacitive performance of EDLCs or ideal capacitor (V Wardani et al, 2020). From figure 7, sample 1 and sample 3 has almost similar pattern of triangle with sample 3 has highest working voltage compare to sample 1. The sample 2 has the larger triangle shape with lowest working voltage. Three graphs indicate the potential of ideal EDLCs with stable electrochemical performance.

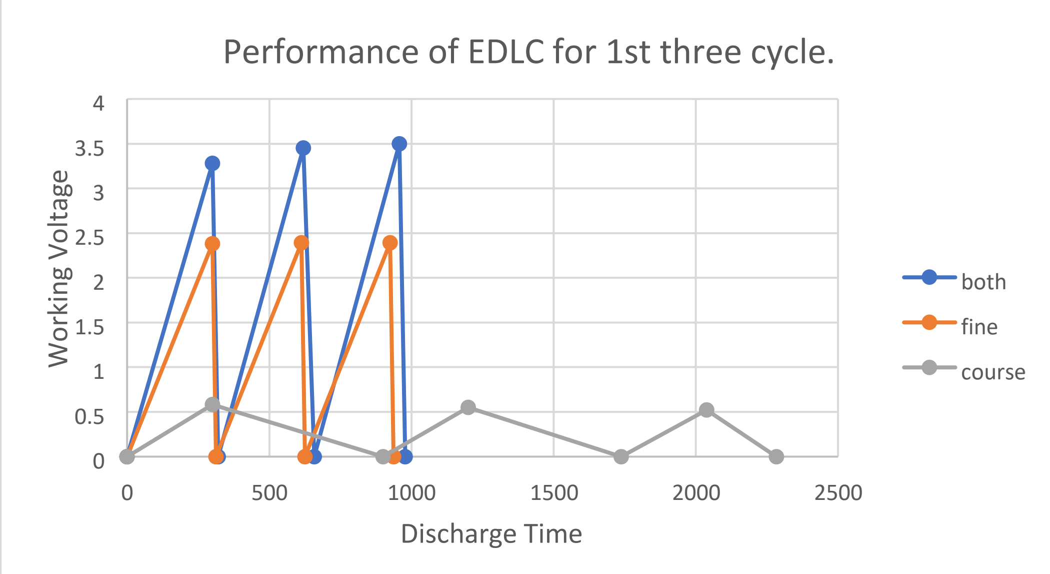

Figure 7: The Charge Discharge pattern for sample 1, sample 2 & sample 3 charge by 4V power supply within 300s charging time.

4. DISCUSSION

4.1 Electrochemical properties of EDLCs

The electrochemical performance for each sample is calculated and recorded as Table 3.

As shown in Table 3, the supercapacitor for Sample 3 Activated Carbon as electrode exhibit the highest capacitance 2952.4 mF and specific capacitance is 1230.16 mF/g as compared to other sample of AC as electrode. The value of capacitance for Sample 1 is lowest which is 26.27 mF and specific capacitance is 21.89 mF/g. This was assumed due some electrolyte ion trapped in the AC pore causes the active site of activated carbon for ion storage decrease which tend to low value of capacitance (O.E. Eleri et al, 2023). Besides that, the other factor such as electrolyte, impurities and side reaction between carbon might decrease the cell capacitance (Krzysztof Kierzek et al, 2020) .

Next, the energy density for Sample 3 is highest with 226.38 Wh/kg as compared to Sample 1 is 17.22 Wh/kg which is more than 8 times higher. The higher energy density show that it has potential as superior quality as supercapacitor (Lin et.al, 2014)

Table 3: Analysis performance of sample for EDLCs.

Sample	Sample 1	Sample 2	Sample 3
Capacitance (mF)	26.27	2672.38	2952.4
Specific Capacitance (mF/g)	21.89	1113.49	1230.16
Energy Density (Wh/kg)	17.22	52.38	226.38

4.2 Electrochemical Analysis for Asymmetric EDLC (Sample 3)

Table 4. The electrochemical properties for the first 10 cycles of supercapacitor charged with V=4V for 5 minutes and assemble in 1.0M KOH as electrolyte.

Cycle	Working Voltage	Discharge Time	Capacitance (mF/g)	Energy density (Wh/g)
1	3.28	20	40.5	0.2181
2	3.45	38	69.6	0.4143
3	3.5	20	35.6	0.2181
4	3.55	22	38.1	0.2399
5	3.66	31	50.5	0.3380
6	3.71	39	61.8	0.4252
7	3.73	39	61.1	0.4252
8	3.72	39	61.5	0.4252
9	3.72	41	64.6	0.4470
10	3.71	51	80.8	0.5561

The table 4 show the discharge time for 1st- 5th cycle is short with average discharge time of 26.2s. This is due to the inadequate time for electrolyte diffusion to happen properly (E. Elanthamilan et al,2019). Then, as the cycle increases, the discharge time also increases gradually with discharge time of 51s at cycle 10th. The value of capacitance during 10th cycle is 80.8 mF/g.

Table 5. The electrochemical properties for the next 8 cycles of supercapacitor charged with V=4V for 5 minutes and assemble in 1.0M KOH as electrolyte.

Cycle	Working Voltage	Discharge Time	Capacitance (mF/g)	Energy density (Wh/g)
11	3.7	68	108.3	0.7414
12	3.68	99	159.4	1.0795
13	3.67	127	205.6	1.3848
14	3.65	152	248.8	1.6573
15	3.64	180	296.3	1.9626
16	3.63	195	322.7	2.1262
17	3.63	214	354.2	2.3334
18	3.48	210	378.1	2.2898

The supercapacitor continued undergo charge discharge processes, enhancement of discharge time with decreasing of working voltage can be seen in the next cycle indicates the supercapacitor operates in low voltage due to the limitation by the thermodynamic stability range of an aqueous electrolytes (F. Juarez et al, 2008*)*. The performance of supercapacitor improved until cycle 17th with even slower discharge time, 214s. As supercapacitor, the cells exhibit the stable and better supercapacitive performance which is until 18th cycles less than 2% the value of capacitance loss.

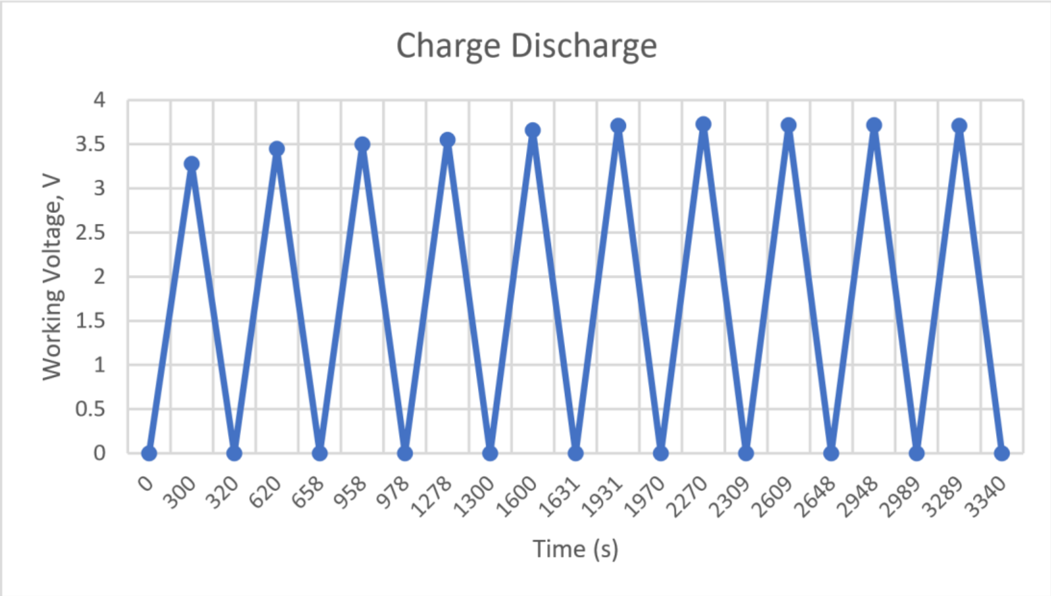

Figure 8. Charge Discharge Graph Voltage versus times are shown for ten cycles.

The Figure 8 shown the charge discharge graph for 10th cycles has symmetric triangle for ideal EDLC supercapacitor. This typical pattern of graph for the activated carbon electrode shows a capacitive behavior with ionic liquid electrolyte (T. D. Larasati et.al, 2019). This indicates the supercapacitor's electrode material being highly conducted. Then, the stability of charge discharge increasing by time. This observation proved that the supercapacitor has good capacitive performance with potential of high cycle life.

5. CONCLUSION

The activated carbon produced by oil palm kernel shell has potential to be developed as supercapacitor energy storage device. In this work an activated carbon-based simple supercapacitor was successfully fabricated. The analysis revealed that the value obtain for capacitance for Sample 1 is 26.3mF, specific capacitance 21.58mF/g and energy density 17.22Wh/kg while the Sample 2 of activated carbon is 2672.38mF, 1113.49 mF/g and energy density 52.384Wh/kg and Sample 3 is 2952.5mF, specific capacitance 1230.16mF/g and energy density 226.34Wh/kg. As conclusion, a high-performance capacitor is achieved by using a asymmetric size of AC by improved the working voltage, discharge time and cycle life.

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References

Aziz, H., Norita Tetra, O., Alif, A., dan Yola Azli Perdana Jurusan Kimia, S., & Andalas Padang, U. (2017). Performance Karbon Aktif Dari Limbah Cangkang Kelapa Sawit Sebagai Bahan Elektroda Superkapasitor Performance Of Activated Carbon From Waste Of Palm Oil Cangcang As Supplementary Superacapapitor. Jurnal Zarah, 5(2).

Chuayboon, S., & Abanades, S. (2022). Continuous solar-driven gasification of oil palm agricultural bio waste for high-quality syngas production. Waste Management, 154, 303–311.

Papilo, P., Marimin, M., Hambali, E., Machfud, M., Yani, M., Asrol, M., Evanila, E., Prasetya, H., & Mahmud, J. (2022). Palm oil-based bioenergy sustainability and policy in Indonesia and Malaysia: A systematic review and future agendas. Heliyon, 8(10).

Portet, C., Yushin, G., & Gogotsi, Y. (2008). Effect of Carbon Particle Size on Electrochemical Performance of EDLC. Journal of The Electrochemical Society, 155(7).

Rennie, A. J. R., Martins, V. L., Smith, R. M., & Hall, P. J. (2016). Influence of particle size distribution on the performance of ionic liquid-based electrochemical double layer capacitors. Scientific Reports, 6.

Adekola, F.A. & Adekoge , H. I. (2005). Adsorption of Blue on activated carbon from rice husk, coconut shell and coconut coirpith. Ife Journal of Soc. Nigeria, 7(1); 151-157.

Sung, K., Watanabe, N., & Kawamura, K. (2015). Experimental results of series or parallel changeover system using battery with EDLC for electric vehicle. 9th International Conference on Power Electronics - ECCE Asia: "Green World with Power Electronics", ICPE 2015-ECCE Asia.

Sutarsis, & Chang, J. K. (2021). Improving the Electrochemical Performances of Supercapacitors through Modification of the Particle Size Distribution of the Carbon Electrode. IOP Conference Series: Earth and Environmental Science, 927(1).

Yamagata, S., Oda, Y., Tanai, M., & Sung, K. (2014). An electric vehicle project for ECO-RUN Race. 2014 International Power Electronics Conference, IPEC-Hiroshima - ECCE Asia 2014.

V Wardani, L Rohmawati , W Setyarsih , D Alfarisi & A Subhan (2020). Analysis of Charging/Discharging Supercapacitor Active Carbon/rGO Based on Natural Materials. Journal of Physics: Conf. Series 1491 (2020) 012044 IOP Publishing doi:10.1088/1742-6596/1491/1/012044.

Elanthamilan et al., "Couroupita guianansis dead flower derived porous activated carbon as efficient supercapacitor electrode material," Mater Res Bull, vol. 112, pp. 390–398, Apr. 2019, doi: 10.1016/j.materresbull.2018.12.028.

Juarez et al., "Fluid Coke Derived Activated Carbon As Electrode Material for Electrochemical Double Layer Capacitor," 2008. [Online].

T. D. Larasati, T. Prakoso, J. Rizkiana, H. Devianto, P. Widiatmoko, and I. Nurdin, "Nano Carbon Produced by Advanced Mild Hydrothermal Process of Oil Palm Biomass for Supercapacitor Material," IOP Conf Ser Mater Sci Eng, vol. 543, no. 1, 2019, doi: 10.1088/1757-899X/543/1/012031.

Obinna Egwu, Eleri Frederik, Huld Julie, Pires Wakshum, Mekonnen Tucho, Philipp Schweigart & Ann Mari (2023). Revealing mechanisms of activated carbon capacity fade in lithium-ion capacitors. Electrochimica Acta 453.

Kierzek K, Gryglewicz G. Activated Carbons and Their Evaluation in Electric Double Layer Capacitors. Molecules. 2020 Sep 16;25(18):4255. doi: 10.3390/molecules25184255. PMID: 32947979; PMCID: PMC7571157

Lin, TW., Dai, CS. & Hung, KC. High Energy Density Asymmetric Supercapacitor Based on NiOOH/Ni3S2/3D Graphene and Fe3O4/Graphene Composite Electrodes. Sci Rep 4, 7274 (2014). https://doi.org/10.1038/srep07274