

Coconut Shell Activated Carbon Super Capacitor Using Various Aqueous and Organic Electrolytes to Enhance Electrochemical Pseudocapacitance

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Abstract. Super Capacitor (SC) has gain momentum as energy storage and provide alternative to rechargeable battery specifically in area where fast charging and burst energy transfer is demanded. SC is also superior in number of charge cycling capability compare to batteries. However in terms of energy capacity SC is still fall short to popular Li-ion battery (a couple of mWh/kg vs few hundreds mWh/kg). In this research we fabricated SC from coconut shell activated carbon and study the result of energy capacity yield when using combination of electrolytes and MnO₂ powder to maximize Electrochemical Pseudocapacitance effect. The electrodes are cut 20x5 cm² and using 70wt% of coconut shell activated carbon (CSAC) mixed with 30wt% polyurethane. The result table indicates that electrolyte of choice can have a significant effect on total SC energy capacity.

1. Introduction

Nowadays more people are using scooters, electric cycles, electric cars, and electric buses. All this electric haulages includes in them electric motors to move the vehicles and off course also brakes to stop them. This counteracting action is a waste of energy, and it can be a huge twenty to thirty percent of movement energy lost for typical transport and can be up to eighty percent of energy lost as friction on heavy traffic [1].

Fortunately with the right kind of motor the movement energy can be converted back to electricity, however this requires energy saving device which can quickly absorbs the momentous burst of power. Battery it is not very useful for this purpose because battery [2] requires a chemical process which is relatively a slow activity. The answer is super capacitor, this device can store quickly the energy equivalent to thousands of regular electrolytic capacitor.

2. Literature Review

How super capacitor can achieve such tremendous capacity lies on the physical factor. Unlike electrolytic capacitor which using flat surfaces to collect electrons on the electrodes plates, super capacitors are using rough surfaces on nano scales [3]. One of the naturally occurring nano scale rough surfaces are activated carbons. Activated carbons, was a biological cellular structures, due to the hot scorching process, all of the hydrogen and oxygen atoms have been vanished to the air, leaving carbons and trace elements, but the original cellular structures have remaining intact, leaving empty pockets which have previously filled by molecules (which had abundance of hydrogen and oxygen atoms). Measurement of surfaces using gas diffusion process have resulted in an equivalent of more than 1000 m² area per gram of carbon active material. So if this stuff is compared with electrolytic capacitor, we



can have thousand time capacity increase. We can expect capacity to super capacitors in the order of tens of thousands of Farads. Application of activated carbon for super capacitor requires pore size around 2-10 nm which is a majority size on CSAC [4]. We can see the prospect for Pseudo capacitive super capacitor in figure 1.

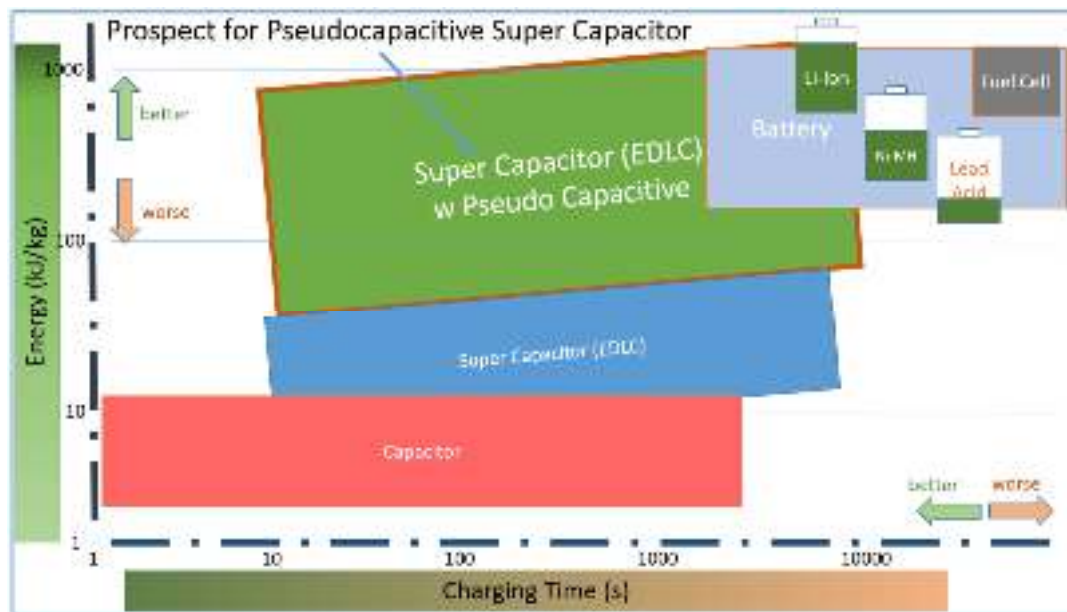


Figure 1. Pseudo capacitance potential for storing energy [5]

One of the method to measure characteristic of SC is called a Cyclic Voltammetry (CV). This method is basically to ramp up voltage given to SC linearly with time until some value and then ramp back down until some less value, then cycle back again. We can see plot of CV for pseudo capacitance which is recognizable, see figure 2.

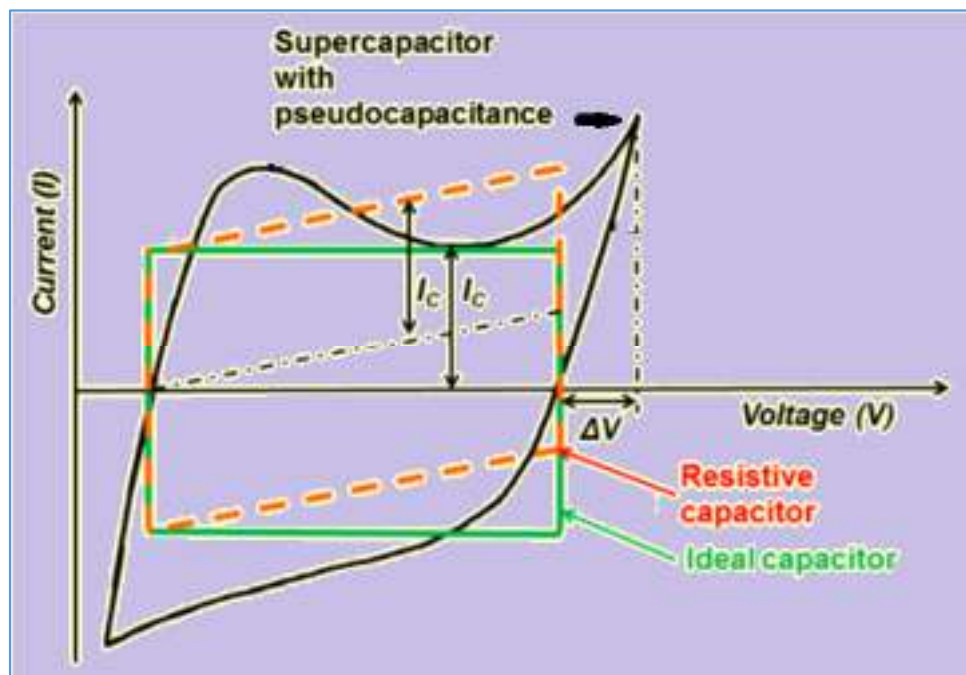


Figure 2. Pseudo capacitance super capacitor potential CV

2.1. Coconut Shell Activated Carbon

Activated carbon is a type of allotropes of carbon for which have a very high porous area. This area can be made by low temperature burning process with chemicals such as H_3PO_4 (Phosphoric Acid) [6]. Activated carbon generally consist of micro pores with some meso pores and macro pores.

The equivalent circuit model of CSAC where deep pores with small diameter is a lot larger will have high internal ESR but also high capacity. It can be shown on the equivalent circuit as in figure.3

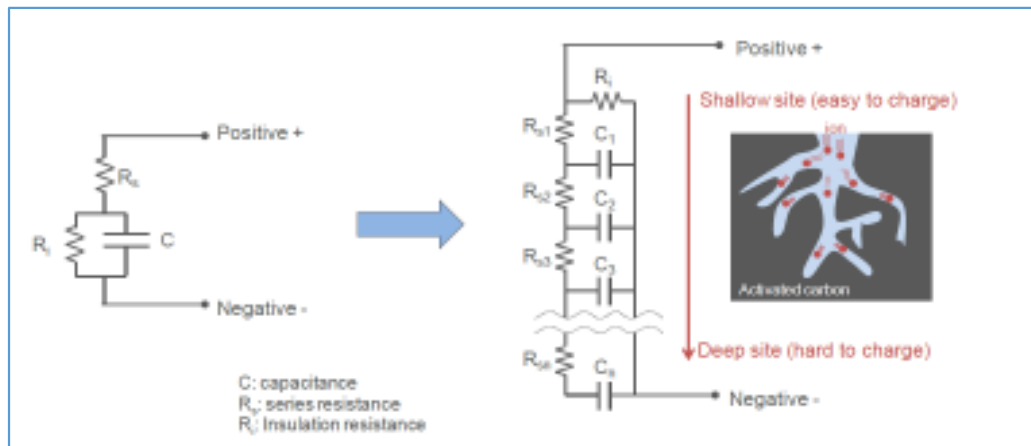


Figure 3. Equivalent circuit for activated carbon/CSAC

2.2. Pseudo Capacitance

Pseudo capacitance (PC) can manifest into 3 types of mechanism: 1. under potential deposition, 2. Redox Pseudocapacitance, 3. Intercalation Pseudocapacitance [7]. Unlike regular EDLC, PC electrode can be made not only from carbons, but also from metal oxides, and conducting polymer. PC capacity can be many fold than that of capacitance of ELDC only, about 10-100 times higher. But the power performance of PC is lower than that of an EDLC because the slower Faradaic mechanism will likely to effect on shrinking and swelling during charging and discharging which will lead to poorer number of total cycles and less mechanical rigidity.

For the experiment, we are focusing on Pseudocapacitance effect of amorphous $MnO_2 \cdot nH_2O$ in KCl aqueous electrolyte. Why we are using MnO_2 [3] because this material is the only abundant element and low cost compare to other elements such as Au or RuO_2 which can induce Pseudocapacitance effect on EDLC[5]. The reaction would be as follow:



Where A is a type of alkali metal, in this experiment instead of using Li or Na we are using Potassium for easy availability reason in the form of KCl. This experiment had been performed first time by Lee and Goodenough [6], on the case of redox reaction with $x=1$, we can then write down the reaction as follow:



Theoretically this reaction will give >1000 F/g, but it was known then that the reaction only took place in a very thin layer of MnO_2 particles since the conductivity of MnO_2 is poor compare to RuO_2 or Gold. This is equivalent to a relatively big value of internal ESR.

2.3. Aqueous and organic electrolyte

Although we have prepared organic electrolyte such as Acetonitrile (AN), but this will not be considered the focus of the experiment, since we are using MnO_2 [5] which only will react to Potassium for the PC

effect. But on the same setup we are conducting the experiment with AN as electrolyte as comparison [8].

2.4. Preparation

For the experiment we prepare as follows: Inventories: isopropyl alcohol (local), Aluminum slabs 200x50x3mm (local), Acetonitrile (AN) (Merck), KCl (local), Polyurethane (local), Coconut Shell Activated Carbon granules 5% moisture max iodine 1062 ug/g (local), Graphite powder (local), MnO₂ powder (Merck), Phosphoric Acid 85% (CHN) and Cellulose Papers (local), Distilled water.

2.5. Experiment

We suspect that we need some graphite to increase conductivity of CSAC, but to be able to see the effect of the percentage of graphite to CSAC[4], we divided the experiments into four formulas (F0-F4) as follows. The experiments were as follows: Pour about 100 grams of CSAC into mixer, grind it at middle speed about 5 minutes, the result would be a very fine powder of CSAC. We will only use portion of this during all the experiment. Put it on a sealed container.

Now we need a mediator to make the fine powder of CASC stick permanently to Aluminum Slab, for this purpose we mix CSAC powder, polyurethane and graphite powder in a glass bowl in a ratio of 3:3.5:3.5, add some isopropyl alcohol as needed to make polyurethane thickness ideal for mixing, add polyurethane hardener about 1/20 part of total polyurethane weight. Mix it with spoon thoroughly on the container for about 3 minutes. As the mixture will be getting harder in minutes we need to apply it immediately to aluminum slab on about $\frac{3}{4}$ of the surface (so the total surface is about 150x50 mm²) this only require a thin layer only. Don't forget to clean the aluminum surface prior the application to make it free from dirt and oil (our hands are oily enough so very important not to touch the cleaned surface).

Add KCl to a distilled water in a high concentration (about 1 full spoon to a 20 ml water). Stir completely for about 1 minute until the KCl powder dissolve completely. Prepare cellulose paper about 3 sheets cut them 200x50mm and put them on top of the prepared aluminum slabs we prepared a day before. Using pipet trickle KCl solution until the papers is completely wet. Then put the other prepared slab on top and press with about 0.5 kg pressure using the iron weight.

Connect the electrodes using alligator clips to charge, discharge machine. Charge the unit to about 0.9v max.

- F0 (formula with 0.0 weight ratio of MnO₂ presence to CSAC)
- F1 (formula with 0.1 weight ratio of MnO₂ presence to CSAC)
- F2 (formula with 0.6 weight ratio of MnO₂ presence)
- F3 (formula Organic Electrolyte Acetonitrile with 0.0 weight ratio of MnO₂ presence)
- F4 (formula with 0.0 weight ratio of MnO₂ presence to CSAC and 2mm thickness of CSAC on each electrode).

3. Result

In Figure 4 below, we can see the result for F0 formula with 0.0 weight ratio of MnO₂ presence to CSAC in comparison with F1 & F2 in the right which has MnO₂ presence as enabler for pseudocapacitance [5], they actually gave almost similar result on charge discharge cycle. However F0 is saturated more rapidly due to less capacitance in pure CASC.

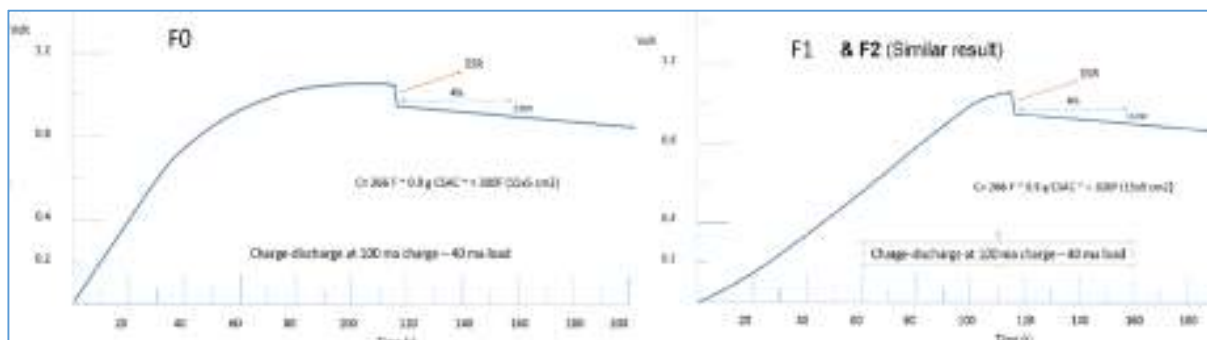


Figure 4. Result for F0, F1 & F2

Where as in Figure 5 we can see that F3 which is a pure organic electrolyte, we can see that this AN electrolyte is capable of accumulating voltage up to 2.65 volts. Translating to a more total energy can be save in the capacitor compare to other formulas (2.65 volt:0.95 volt -> about 2.7 times more capacity), but AN is more expensive and toxic than aqueous electrolyte. On F4 we can see the ESR is too high due to the thick of the CASC layer (2 mm vs. 0.03 mm on formula F0, F1, F2 & F3).

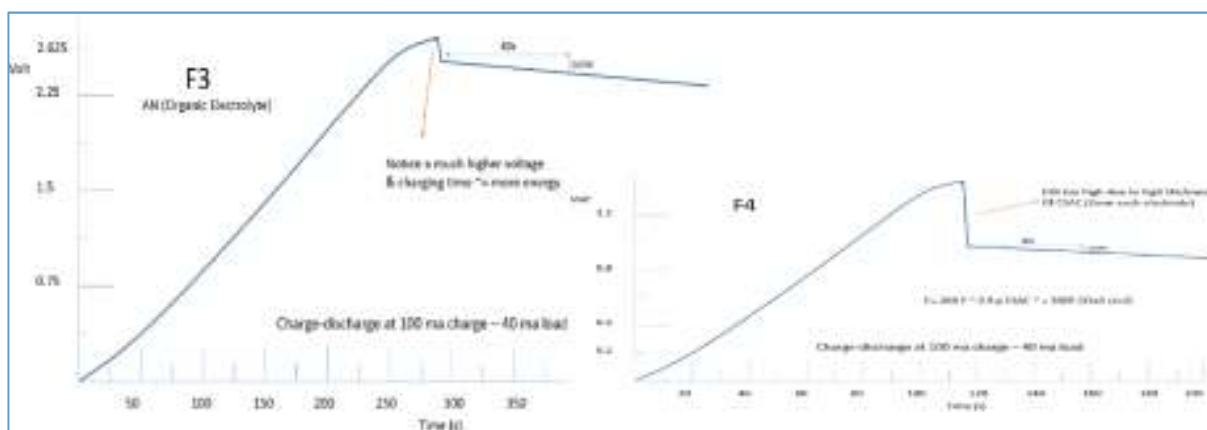


Figure 5. Result for F3 & F4

4. Discussion & Conclusion

From the result above we can conclude: CSAC can be made into workable SC in the form of a thin layer of the material mixed with adhesive, if more than 100 micron thick might need to have conductive material to enhance conductivity (in this experiment was graphite). Pseudo capacitance can be made using less precious metal such as Manganese, but this might not be the best solution if the purpose was to provide maximum capacity, since Mn has poor conductivity compare to other transition metal which exhibit PC effect such as Ruthenium and gold. But further study might enhance result with different variation allotropes of Mn. Organic Electrolyte is superior for total capacity resulted with the same configuration of CSAC physical setup compare to aqueous electrolyte. This to the effect of working voltage of the electrolyte is higher. Organic Electrolyte so far is not very useful when paired with Mn to be able to get pseudo capacitance effect on SC.

5. References:

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