Characteristics Analysis of Carbon and Metal Oxidesbased Electrode Materials

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ABSTRACT

Tendifferent supercapacitors were fabricated to see the influence of hybrid configuration on supercapacitor performances, the electrode configurations were set up using carbon electrode as anode and metal oxide electrode as cathode. In the cathode electrode a combination of two from these three different transition metals where used Cobalt (Co),Nickle (Ni)and Manganese (Mn). The different transition metal combinations obtained made it possible to see the effect it has on specific capacitances.The samples were labeled from sample 1 to sample 10. The obtained Cyclic Voltammetryplots were used to calculate specific capacitance of each cell and comparison of results were made with other samples. The highest specific capacitance value obtained was $78Fg^{-1}$for sample 9 and the minimum value obtained was $5Fg^{-1}$ for sample 10.

Keywords: Supercapacitor, Metal Oxide, Cyclic Voltammetry, Specific Capacitance.

1. INTRODUCTION

Supercapacitor also known as electrochemical supercapacitor or ultracapacitor technology has come a long way since the first patent was filed in 1957. Supercapacitor is a devices used for energy storage, whose characteristics are between those of conventional capacitors (dielectric capacitors) and batteries. Important form of energy cannot be fully utilized without advancements in electrical energy storage (EES). Supercapacitor and secondary batteries are the two main types of EES devices [1]. Recent research works have focused on ways of improving the efficiency and also the power output of supercapacitor, due to the growth of technologies required in the production of better and more sophisticated devices.

A supercapacitor consists of two electrodes, an electrolyte, and a separator that electrically isolates the two electrodes. The most important component of a supercapacitor is the electrode material [2]. Some of the benefits of supercapacitors when compared with other energy storage devices are high power capability, long life, wide thermal operating range (-40ºC to 70ºC), low weight, flexible packaging, and low maintenance [3]. Supercapacitors can best be utilized in areas that require applications with short load cycle and high reliability, for example energy recapture sourcessuch as load cranes, forklifts, and electric vehicles, power quality improvement [4]. Among the promising applications of supercapacitors is in fuel cell vehicles and low emission hybrid vehicles [5]. Supercapacitors with its unique qualities when coupled with primary high energy batteries or fuel cells they can serve as temporary energy storage devices with a high power capability to store energies when braking [6]. Despite the numerous benefits derived from using supercapacitors, some of its drawbacks include- low energy density compared to batteries, high production cost, high self-discharge and low voltages.

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Due to its high power capability a bank of supercapacitors, can bridge the short time duration between a power failure and the start up of backup power generators. While the energy density of supercapacitors is very high compared to conventional dielectric capacitors, it is still significantly lower than batteries or fuel cells. Electrochemical performances of an electrode material strongly rely on factors like surface area, electrical conductivity, wetting of electrode and permeability of electrolyte solutions [7]. The most commonly used electrode materials are Activated Carbon, Metal Oxides and Conducting Polymer.

In general, considering energy storage mechanism, supercapacitors are classified into two categories. First is the electrical double layer capacitor (EDLC), capacitance is obtained from pure electrostatic charge accumulated at the electrode/electrolyte interface; therefore it strongly depends on the surface area of the electrode materials that is accessible to the electrolyte ions. Second is the pseudo-capacitor, in this case a fast and reversible faradic process take place due to electro active species [8], [9].

There are various ways of determining the efficiency of a Supercapacitor, some of which include; Electrochemical Impedance spectroscopy (EIS), cyclic voltammetry (CV) and galvanometric analysis.

2.   METHODOLOGY

2.1. Preparation of carbon electrode

The supercapacitor fabricating cell consists of a carbon electrode and a metal- oxide electrode, separated by a permeable material; hence the carbon electrode must be prepared in the lab using three different compounds namely; activated carbon, Black carbon (XL6) and Polyvinylidene fluoride (PVDF). A binder is required to bind the two carbon particles properly, hence the use of PVDF which is relatively cheap and reliable. A polar solvent known as N-Methylpyrrolidone (NMP) is used in dissolving the PVDF. Since a total of 3g is required in preparing the electrode, hence the binder constitutes 7% of the material which is 0.0262g, black carbon constitutes 13% which is 0.04875g and the activated carbon which is the most important material constitutes 80% which is 0.24g. The steps involved in preparing the carbon electrode are listed below:

- The three materials are measured using a weighing paper and kept aside.

- The PVDF is poured into a mortar with some drops of NMP solution and continually stirred using a pestle until a slightly thick paste is formed.

- The black carbon is then added to the paste and some drops of NMP solution are added.

- The activated carbon material is then poured in and stirred for a minimum of 5 minutes to ensure that the two carbon materials are well bound.

- A square shaped aluminum foil is prepared with the surface scratched with sand paper to make it coarse so as to enable the paste to stick to it properly.

- The paste is then spread on the aluminum paper and placed in a vacuum oven at 70ºC for 12 hrs.

2.2. Preparation of metal oxide electrode

The same materials are used in preparing the metal oxide electrode with the exception of activated carbon which is replaced with the prepared metal oxide samples. The steps for preparing the carbon electrode are also employed in the preparation of the metal oxide electrode.

2.3. Preparation of metal oxide samples

A total of 10 samples were prepared from a combination of two out of the three transition metals (Co,Ni, and Mn). The metals are combined by varying the degree of inversion by a factor of 0.2 of the combining metals.

Sample 1 $Ni_{0.2}Co_{0.8}Fe_2O_4$: This compound was produced from a combination of Ferric Nitrate "Fe (NO_3). $9H_2O$", Nickel Nitrate Hexahydrate "Ni $(NO_3)_2$. $6H_2O$", Cobalt Nitrate Hexahydrate" Co $(NO_3)_2$. $6H_2O$" and Citric acid "$C_6H_8O_7$". The quantity of each compound to be used is determined by calculating the molar mass and then multiplying by a ratio of 2, 0.8, 0.2 and 4 for each compound respectively. The mass of each compound used was 4.0406g, 0.29081g, 1.16412g and 3.8414g respectively.

The steps involved in sample preparation are listed below;

- The weighed compounds are poured into 4 different beakers and 20ml of methanol is added to each to help in dissolving the compound.

- 100ml of distilled water is then poured into each beaker.

- Each beaker is then transferred to the sonicator, which helps in mixing the compound uniformly.

- All four solutions are gently poured into a 500ml beaker and then placed on the magnetic stirrer whose temperature is set to 150ºC with a speed of 1200rpm, to help in the heating and continuous stirring of the mixture.

- The mixture is covered with aluminum foil with tiny holes and then left in a chimney for 12 hrs.

- The temperature is then increased to 300ºC until the solution forms a thick paste.

- The paste is then put into a "boat" which is going to be transferred to a tubular furnace for the heating process.

Heating Process

The boat is placed in a tubular furnace and the heating process is set using a microcontroller located at the front side. The three important variables to be set include; ramping rate (the rate at which the temperature increases with time), the set point (target temperature) and the dwell time. The heating process is divided into 5 stages.

- The temperature of the furnace is increased to 150^0C by setting the ramping rate to 20ºC / min, the set point to 150ºC and the temperature is maintained for 30 minutes by setting the dwell time to 30.

- The second stage involves increasing the temperature to 350ºC using the same set point and dwell time

- The temperature is then increased to 450ºC with the dwell time maintained

- Finally the temperature is ramped to 600ºC with the same ramping interval and the dwell time is set to 6hrs.

- The final stage is known as the cooling down process which is between 7-8 hrs.

The dry substance obtained after the heating process is then poured into a mortar and then grounded into small sized particles. Figure below shows some of the prepared samples stored in a plastic container.

The same procedures used in sample preparation and heating process is employed for other metal oxide combinations, the difference been the mass of compound used.

Sample 2 $Ni_{0.4}Co_{0.6}Fe_2O_4$: The molar masses of Ferric Nitrate, Nickel Nitrate Hexahydrate, Cobalt Nitrate Hexahydrate and Citric acid were multiplied by factors of 2, 0.4, 0.6 and 4 respectively. The mass of each compound used was 4.0406g, 0.58162g, 0.87309g and 3.8414g.

Sample 3 $Ni_{0.6}Co_{0.4}Fe_2O_4$: The molar masses of Ferric Nitrate, Nickel Nitrate Hexahydrate, Cobalt Nitrate Hexahydrate and Citric acid were multiplied by factors of 2, 0.6, 0.4 and 4 respectively. The mass of each compound used was 4.0406g, 0.87243g, 0.58206g and 3.8414g.

Figure 1: Prepared Sample.

Sample 4 $Ni_{0.2}Mn_{0.8}Fe_2O_4$: The same compounds used in producing the above named samples are used with the exception of Cobalt Nitrate Hexahydrate" Co $(No_3)_2$. $6H_2O$", which is replaced by Manganese (II) Nitrate Hexahydrate "Mn $(NO_3)_2$. $6H_2O$". The molar mass of Manganese Nitrate Hexahydrate is 287.04 g/mol and the mass used in preparing the solution is 1.14816g. The molar mass was multiplied by a factor of 2, 0.2, 0.8 and 4 respectively. The mass of each compound used was 4.0406g, 0.29081g, 1.14816g and 3.8414g.

Sample 5 $Ni_{0.4}Mn_{0.6}Fe_2O_4$: The molar masses of Ferric Nitrate, Nickel Nitrate Hexahydrate, Manganese (II) Nitrate Hexahydrate and Citric acid were multiplied by factors of 2, 0.4, 0.6 and 4 respectively. The mass of each compound used was 4.0406g, 0.58162g, 0.86112g and 3.8414g.

Sample 6 $Ni_{0.6}Mn_{0.4}Fe_2O_4$: The molar masses of Ferric Nitrate, Nickel Nitrate Hexahydrate, Manganese (II) Nitrate Hexahydrate and Citric acid were multiplied by factors of 2, 0.6, 0.4 and 4 respectively. The mass of each compound used was 4.0406g, 0.87213g, 0.57408g and 3.8414g.

Sample 7 $Mn_{0.2}Co_{0.8}Fe_2O_4$: The molar masses of Ferric Nitrate, Cobalt Nitrate Hexahydrate, Manganese (II) Nitrate Hexahydrate and Citric acid were multiplied by factors of 2, 0.8, 0.2 and 4 respectively. The mass of each compound used was 4.0406g, 1.16412g, 0.28704g and 3.8414g.

Sample 8 $Mn_{0.4}Co_{0.6}Fe_2O_4$: The molar masses of Ferric Nitrate, Cobalt Nitrate Hexahydrate, Manganese (II) Nitrate Hexahydrate and Citric acid were multiplied by factors of 2, 0.6, 0.4 and 4 respectively. The mass of each compound used was 4.0406g, 0.87309g, 0.57408g and 3.8414g.

Sample 9 $Mn_{0.6}Co_{0.4}Fe_2O_4$: The molar masses of Ferric Nitrate, Cobalt Nitrate Hexahydrate, Manganese (II) Nitrate Hexahydrate and Citric acid were multiplied by factors of 2, 0.4, 0.6 and 4 respectively. The mass of each compound used was 4.0406g, 0.58206g, 0.86112g and 3.8414g.

Sample 10 $Co_{0.2}Mn_{0.8}Fe_2O_4$: The molar masses of Ferric Nitrate, Cobalt Nitrate Hexahydrate, Manganese (II) Nitrate Hexahydrate and Citric acid were multiplied by factors of 2, 0.2, 0.8 and 4 respectively. The mass of each compound used was 4.0406g, 0.29103g, 1.14816g and 3.8414g.

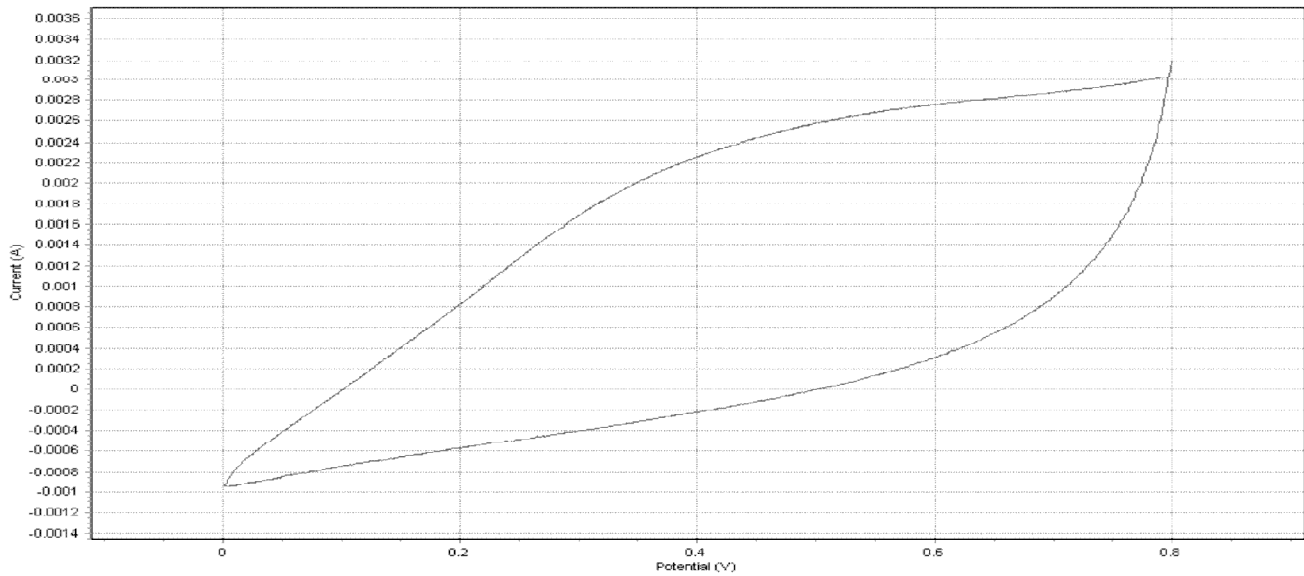# 3.   RESULTS AND DISCUSSIONS

3.1. Sample 9 (Mn$_{0.6}$Co$_{0.4}$)

Figure 2: Cyclic Voltammogram of Sample 9

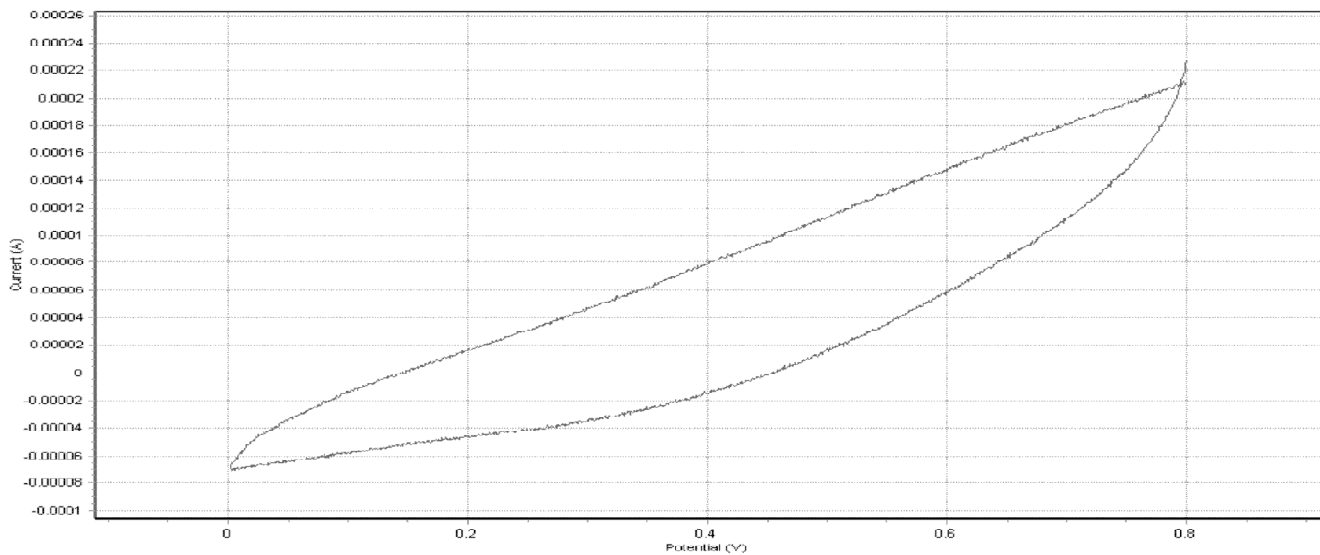## 3.2. Sample 10 (Mn$_{0.8}$Co$_{0.2}$)

Figure 3: Cyclic Voltammogram of Sample 10

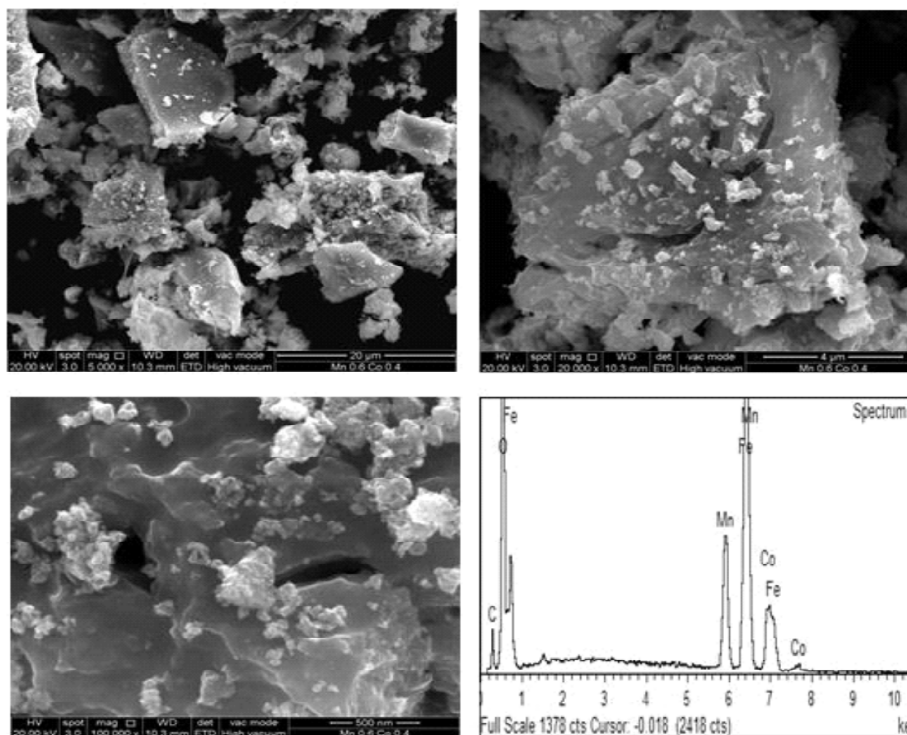## 3.3. Sample 9($Mn_{0.6}Co_{0.4}$)

Figure 4: (top left) SEM image at 5000x, (top right) SEM image at 20000x, (bottom left) SEM image at 100000x, (bottom right) EDX plot
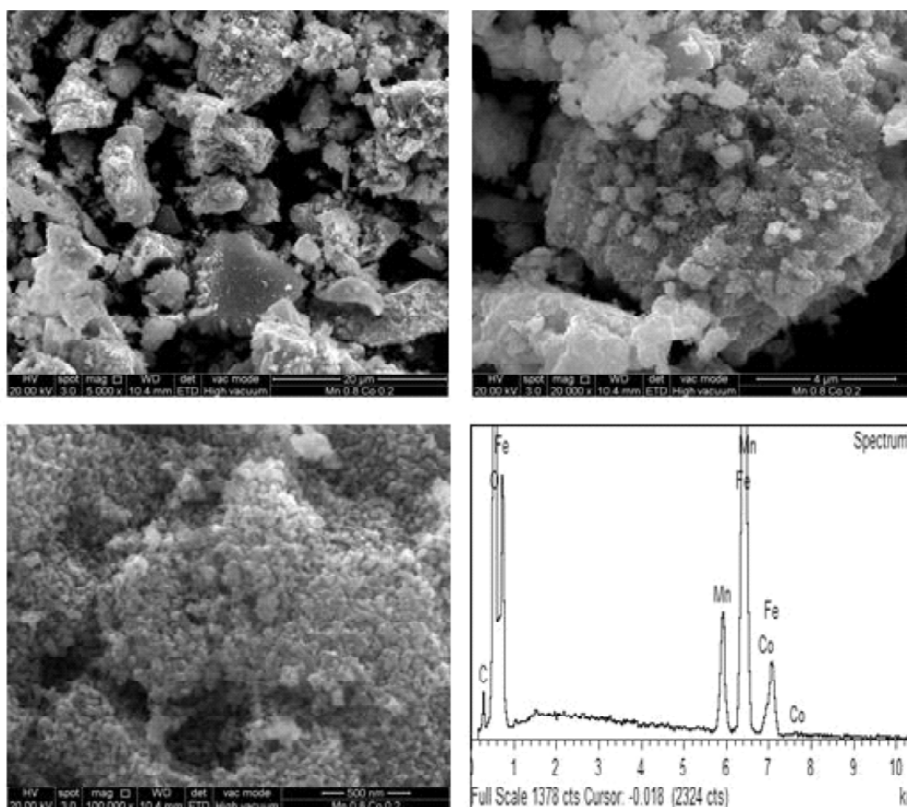
3.4. Sample 10($Mn_{0.8}Co_{0.2}$)

Figure 5: (top left) SEM image at 5000x, (top right) SEM image at 20000x, (bottom left) SEM image at 100000x, (bottom right) EDX plot

The performance and measurement of the fabricated supercapacitor was determined using CV analysis which was used for calculating the specific capacitance of the cell.The specific capacitance of the cell can be calculated by dividing the capacitance by the weight of the metal oxide in the electrode.

A constant scan rate of 5mV/s was used with a voltage range of 0-0.8V. Initial potential was set to 0V, vertex potential was set to 0.8V and the second vertex potential was set to 0V. A current range of 2mA was used for all Ni_Co combinations and 20mA for Ni_Mn and Mn_Co combinations.

Table 1 gives the summary of the weight of the metal oxide for each cell.

Table 1
Mass of metal oxide in each electrode

Samples	Metal Oxide Sample	Weight (g)
1	$Ni_{0.2}Co_{0.8}$	0.00320
2	$Ni_{0.4}Co_{0.6}$	0.00728
3	$Ni_{0.6}Co_{0.4}$	0.00568
4	$Ni_{0.2}Mn_{0.8}$	0.00464
5	$Ni_{0.4}Mn_{0.6}$	0.00352
6	$Ni_{0.6}Mn_{0.4}$	0.00544
7	$Mn_{0.2}Co_{0.8}$	0.00368
8	$Mn_{0.4}Co_{0.6}$	0.00328
9	$Mn_{0.6}Co_{0.4}$	0.00408
10	$Mn_{0.8}Co_{0.2}$	0.00416

$$Capacitance = \frac{1}{V/dt}$$

$$Specific\,Capacitance = \frac{capacitance}{mass\,of\,metal\,oxide}$$

With the given formula above the specific capacitance for each cell is calculated as shown in the table 2:

Table 2
Specific Capacitance of fabricated cell

Samples	Metal Oxide Sample	Specific capacitance (Fg^{-1})
1	$Ni_{0.2}Co_{0.8}$	10
2	$Ni_{0.4}Co_{0.6}$	38.5
3	$Ni_{0.6}Co_{0.4}$	77.5
4	$Ni_{0.2}Mn_{0.8}$	60
5	$Ni_{0.4}Mn_{0.6}$	11.4
6	$Ni_{0.6}Mn_{0.4}$	22
7	$Mn_{0.2}Co_{0.8}$	10.9
8	$Mn_{0.4}Co_{0.6}$	36.9
9	$Mn_{0.6}Co_{0.4}$	78.4
10	$Mn_{0.8}Co_{0.2}$	5

As it can be seen from Table 2 above the highest specific capacitance was obtained for Sample 9 ($Mn_{0.6}Co_{0.4}$). From the SEM images above it can be observed that the pores obtained are large in size. The large

pore size can be a coalescence process whereby the grown particle increase in size and then come closer to each other. The large pore size makes it suitable as asupercapacitor material because it would easily allow the diffusion of the electrolyte, an important process in the functioning of asupercapacitor, hence the large specific capacitive value obtained.

Likewise from Table 2 above it can be seen that the lowest specific capacitance was obtained for Sample 10 ($Mn_{0.8}Co_{0.2}$). Looking at the SEM images above it can be seen that sample 10 ishaving a non-uniform crystalline image with hairy surface which makes it difficult for electrolyte to pass through it, therefore making itunsuitable as a Supercapacitor material.

CONCLUSION

Based on the experiments carried out the following points were deduced:

- Large pore size made it possible to allow easy diffusion of electrolyte, which yielded large specific capacitance.

- It was noticed that the shape of charge-discharge curves suggest that the capacitance originates from ion adsorption at electrolyte and metal oxide interface.

- It was observed that the hairy surface makes it difficult for electrolyte to pass through.

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