# Insitu carbon coated NaFeO$_2$ as a positive electrode for Sodium Ion batteries.

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*Abstract* :   Due to unique behavior, the Na ion batteries have become a promising candidate for energy storage applications and also the abundant of Sodium Sources on the earth crust. With this point of view, in the present work we report , Insitu carbon coated NaFeO$_2$ gel assisted combustion method. The XRD and Rietveld refinement confirms the phase purity of the prepared material. The SEM images show that the carbon was coated on the outer surface of the cathode material. The carbon enhances the performances of the electrode material and greatly reduces the side reactions occur at the electrode surface. The electrochemical performance was analyzed, the electrode delivers the capacity of about 125 mA h/g and 72 mA h/g at 50 and 3200 A/g current densities and the capacity retention is about 80-90% after 250 Cycles. The results show that cost effective and highly performed electrode for sodium ion Batteries.

*IndexTerms* - :   **Na ion batteries, Insitu, carbon coated, Rietveld, gel assisted.**

## I. INTRODUCTION

With the increasing interest on energy storage applications and the demand on Li source, the great focus was given towards Na ion batteries. Compare to Lithium ion batteries, the cost of Na ion batteries are low because of abundant of Na source on the earth's crust [1-5]. Recently the introduction of hybrid vehicles and large scale electric power storage systems, the great interest was focused on Na ion for large scale energy storage applications [6-8]. As earlier in demonstrating the performance of the full cell which includes sodium intercalation guests in a layered sodium transition metal oxide as the positive electrode and carbon as the negative electrode without using Na metal [8-11]. The main issues of Na ion batteries are the volumetric density and reversible capacity is to be rectified and Na ion batteries have low operating voltages [12]. For improving the performance of the electrode materials, the carbon was coated on the electrode surface , the carbon coated greatly increases the performance of the electrode by increasing the stability by reducing the side reactions occurs on the surface of the electrode [13-14]. Various elements was used as carbon like glucose, citric acid , Multi-walled carbon nanotubes , glycine and oxides like Al$_2$O$_3$ , ZnO , SnO etc are effectively increases the stability of the electrode material.

Layered transition metal oxides, such as lithium cobalt oxide and Lithium magnesium cobalt oxide are generally used as positive electrode for LIBs. Delmas [15] notation says that the structure Li

Containing layered transition metal oxides can be categorized as a so called O3 type structure in which the transition metal slabs stack along the C axis with cubic packed oxygen arrays and the alkali ions occupying the octahedral sites in the inters lab space. Mostly sodium shares most of the chemical and physical properties of Lithium , even though of same structure the operating voltage of NIB is lower than lithium. Therefore $NaFeO_2$ received everyone attention as it as a material with high operating voltage on the basis of the $Fe^{3+}/Fe^{4+}$ redox reaction and it van delivers the capacity of about 80 mAh $g^{-1}$ reversible capacity. In the present work we prepared Insitu carbon coated $NaFeO_2$ through Gel assisted Combustion method.

## II. **Experimental Procedure**.

The positive electrode NaFeO2 was prepared through gel assisted combustion method. The stochiometry amount of Sodium Nitrate and Iron Nitrate was dissolved in water and allowed to stirrer for few minutes until the ions completely dissolves in water. Then Glycine was added to above solution as a chelating agent and also glycine act as a carbon source.The solution was heated to 80 $^0$C . After few hours of stirring the gel formed and finally fluffy powder was obtained. The prepared powder was finally sintered at 700 $^0$C for 10 hrs. The schematic of preparation was shown in the Fig 1.
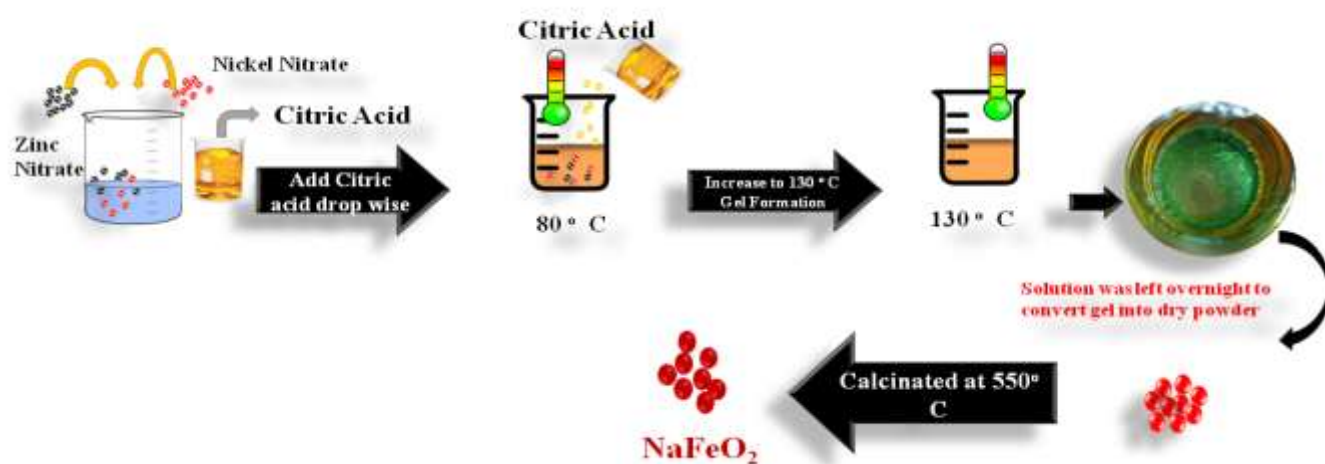


*Insitu Carbon Coated NaFeO₂ through gel combustion method*

## III. Electrochemical  Measurements.

The electrochemical analysis are carried out using CR2032 coin cells are prepared inside a glove box under argon atmosphere. The prepared sample was taken as a cathode and pure Na metal as anode and polypropylene as separator. The electrolyte was prepared by mixing 1M $NaClO_4$ by mixing with EC and DEC( 1:1 v/v ). The cathodes were prepared by mixing 2.5 g of prepared active material with 0.5 g ketjen black and 0.5 mg of teflonized acetylene black     (TAB-2). The prepared mixture was pasted on a stainless steel current collector and dried in the vacuum oven at 160 C before fabricating coin cells. The charge – discharge was performed at different voltages at varying current densities ( 20- 2000 $mAg^{-1}$) using Arbin BT – 2000 battery tester system. EIS analysis were performed using as electrochemical analyzer (SP-150 , Biologic, France).

## IV Materials  Characterization.

Structural analysis  by X-ray diffraction ( XRD  Cu  K radiation, Rint 1000 , Rigaku (Japan) in the range 2Ө of 10-90° lattice parameters and crystal values are calculated by Rietveld Refinement using Full-Prof software. The surface morphology and elemental composition was performed by using scanning electron microscope (Hitachi, Japan) and high resolution transmission electron microscope (HRTEM , JEOL Japan).

## V Results and Discussion

The Phase purity was analyzed by using XRD analysis. The fig 2a shows the XRD pattern of the prepared material Carbon coated $NaFeO_2$. The diffraction peaks of the sample could be assigned to an O3- layered oxide with a space group of R3m. The diffraction shows that the carbon was coated on $NaFeO_2$ which does not change the natural purity of $NaFeO_2$. The diffraction peaks (003), (006),(101),(012),(104)  [16] are well matches with the JCPDS Card num: which shows that no impurity peak was observed. The figure 2b shows the Rietveld refinement spectrum of Carbon coated $NaFeO_2$.

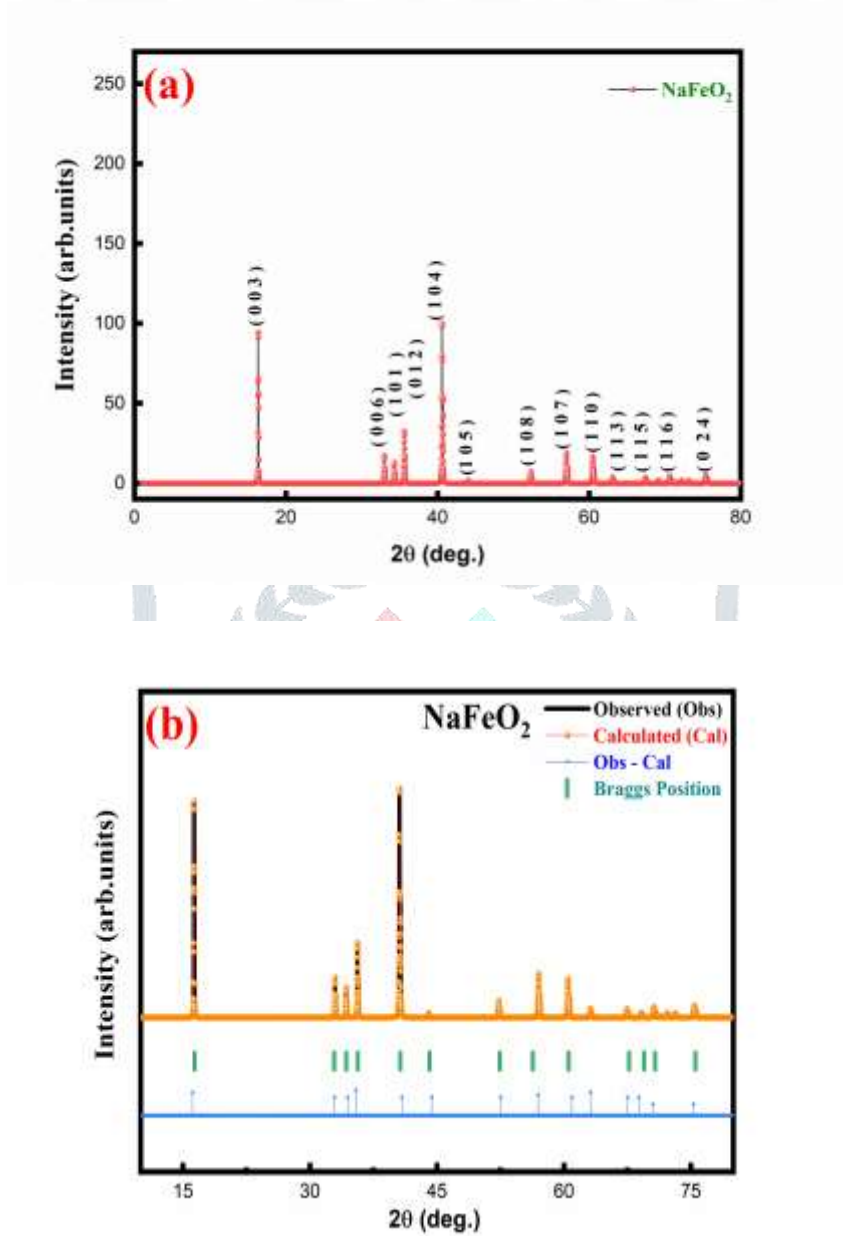| Sample | Phase | Fraction | a(Å) | c(Å) | $R_p$ | $wR_p$ | Gof |
|---|---|---|---|---|---|---|---|
| **Carbon Coated NaFeO₂** | O3 | 92.6% | 3.0535 | 16.133 | 2.233 | 4.05 | 1.24 |
| | C | 7.4 % | | | | | |





Figure 2 (a) the XRD spectra of Carbon coated NaFeO₂ (b) The Rietveld refinement analysis

**Table :1 The Refinement parameter of Carbon coated NaFeO₂**

The Rietveld refinement confirms the phase purity of the material. The refinement results shows that the lattice parameter of the sample . The results shows that the influence of carbon on the surface of NaFeO₂ which increases the crystal structure which was shown in figure 1c. The XRD and Rietveld refinement  The figure 3 shows the FESEM images of  the prepared samples.

## VI FESEM Analysis

The morphological information can be analyzed through FESEM analysis. The figure 3(a. b) shows the FESEM images with different magnification. The FESEM images shows the well defined particles in the nanometer range. The Sponge surface was observed at the surface with minutes pores on the top of $NaFeO_2$, the presence of minute pores are due to two reasons (i) the naturally acquired pores by $NaFeO_2$ (ii) due to carbon presence on the surface of $NaFeO_2$ which shows its influence during electrochemical performance[17].
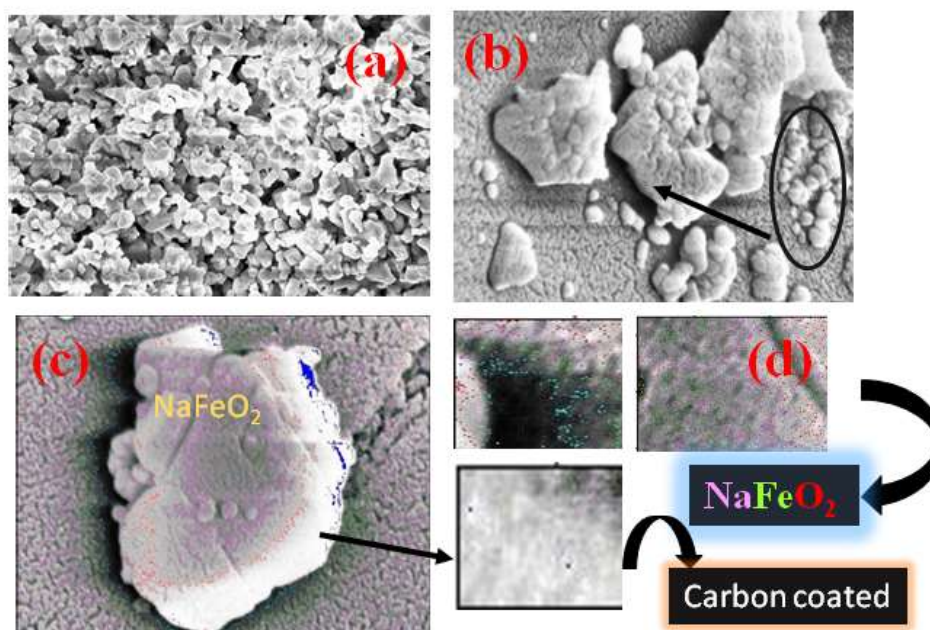


**Figure 3 The FESEM images (a-b) Carbon coated $NaFeO_2$ with different magnification (c-d) presence of carbon on $NaFeO_2$**

The figure 3c shows the single particle magnification of $NaFeO_2$, in which the spongy pores can be clearly seen at high magnification. The figure 3d confirms the presence of $NaFeO_2$ and carbon in the prepared samples which shows the carbon was present only on the surface of $NaFeO_2$. The FESEM results confirms with the XRD results that the carbon was coated on the surface of the $NaFeO_2$ which greatly influences in the performances of the electrode materials during long term cycling and also addition to this , the carbon on the surface creates minute pores on the surface of $NaFeO_2$ which also plays an important role in the performance of the electrode materials.

## VII Electrochemical Analysis

The figure 4 shows the electrochemical performance of the prepared sample. The electrochemical analysis determines the performance of the electrodes. The figure 4a shows the cyclic voltametry curve of

the carbon coated $NaFeO_2$ samples. The CV curves shows that the oxidation and reduction peak was observed at 3.5 v. The peak at 3.5 V and 3.8 V denotes the oxidation peak and the reduction peak was observed at 3.0 V which clearly shows the reversibility of the material. The area of the curve also looks so strong and addition of carbon , after 10 cycles there is no major changes in the area of the curve which intimates the stability of the material during cycling. The addition of carbon clearly shows the influence on the performance of the electrodes during cycling as mentioned earlier in the FESEM analysis. The Cyclic voltametry confirms the reversibility nature of the material during cycling.
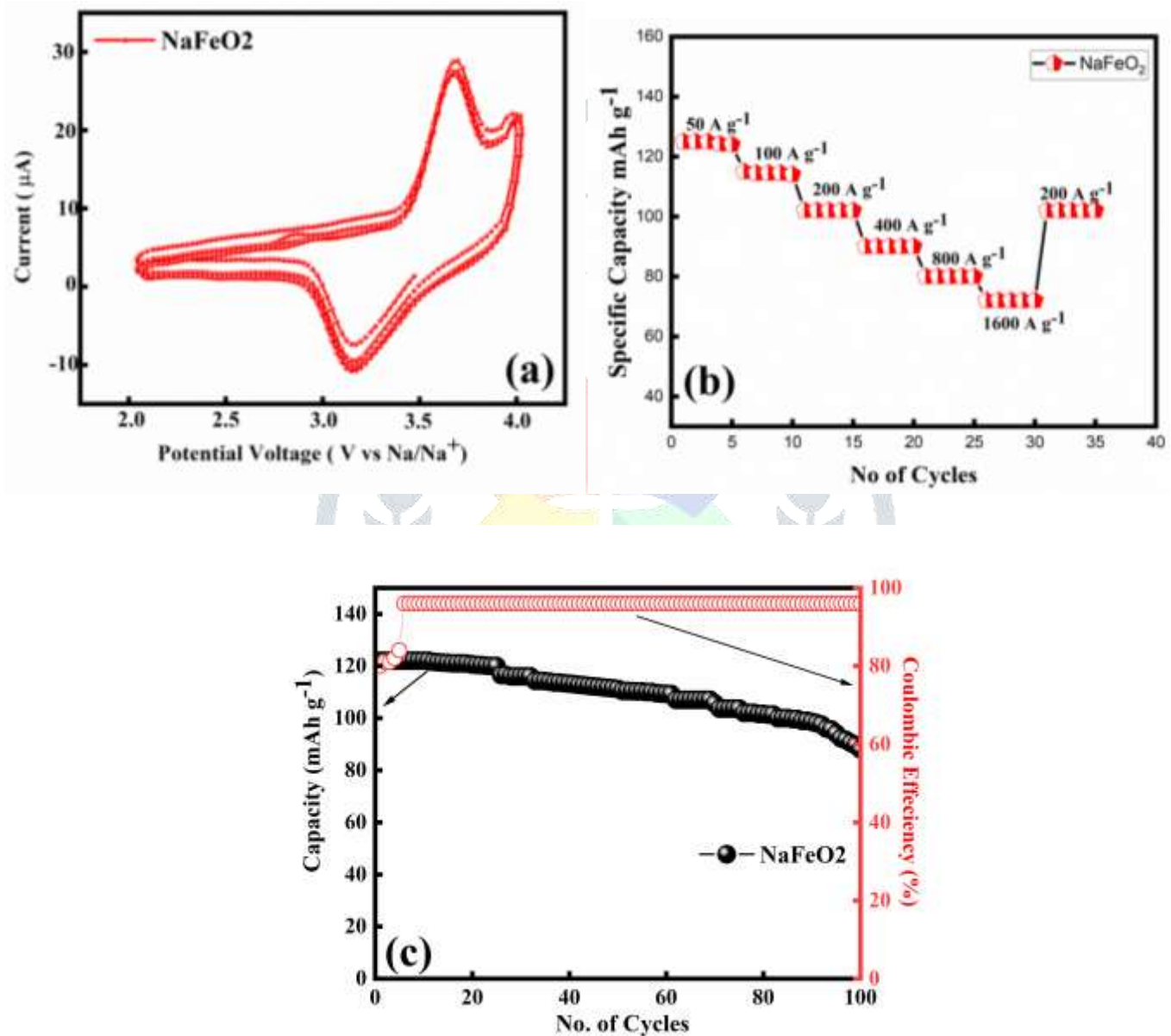


**Figure 4 The electrochemical performance (a) CV spectra (b) Rate performance (c) Cyclic performance (d) impedance spectra of carbon coated $NaFeO_2$**

The prepared electrode materials are performed with different current densities(figure 4b). The electrode delivers the highest capacity of about 126 mAh $g^{-1}$ at 50 $Ag^{-1}$. When the current density increases the capacity decreases so on increasing the current densities from 50 $Ag^{-1}$ , the capacity seems to be

discharged gradually. The capacity values are 126 , 114 , 102 , 90 , 80, 72 mAh g$^{-1}$ at 50 , 100 , 200 ,400 ,800 ,1600 , 3200 Ag$^{-1}$ respectively. Interestingly the capacity seems to decreases but the stability of the materials holds good even at high current densities because of carbon coating on the surface of the NaFeO$_2$ which greatly increases the performance of the electrode .The reason behind the better performance of the electrode is due to carbon on the surface , which created some minute pores in the spongy surface of NaFeO$_2$. These minute pores play a vital role in the performance of the electrode this is because the carbon coating reduces the side reactions occur on the electrode surface. The presence of carbon on the surface with minute pores transport electron between the electrodes. The pores reduces the electron trapping at high operating voltage it results in the smooth transport of ion between the electrodes during cycling. Addition to this diffusion of ions at higher current rates was greatly reduced, results in minimal electrolyte diffusion of ions. Figure 4c shows the cyclic performance and coulombic efficiency of the electrode materials. The electrode materials was cycled for 100 cycles and the capacity retention is about 85% which is comparatively high on comparing with previous reports [18 - 20]. Initially the capacity fade was observed which is due to various phenomena like (i) electrolyte decomposition , which resulted in the formation of a solid-electrolyte interface (SEI) layer [21], (ii) Jahn – Teller distortion resulting in Fe$^{2+}$ dissolution into the electrolyte[22] ,(iii) several internal stress with a significant volume change resulting in the accommodation of larger size Na ions [23], (iv) insertion of solvated ions into the metal oxide layers[24], the carbon coating increases the stability of the material during long term cycling process. The capacity retention is about 85-90% and the coulombic efficiency is about 97%. The electrochemical results show that the carbon on the surface greatly increases the performance of the electrode materials.

To further evaluate the kinetic properties, EIS was used as a major tool. Fig. 4d shows the Nyquist plots of carbon coated NaFeO$_2$ before and after cycling. The plot exhibits three regions, with a depressed semicircle in the high-frequency region, followed by a semicircle in the high to medium frequency, and a quasi-straight line in the low frequency region, corresponding to the surface resistance (SEI layer), charge transfer resistance (Rct), and Warburg impedance, respectively [25]. Obviously, the charge transfer resistance is very much reduced for the Carbon coated sample, compared to that of the without carbon coated material. This is due to the rapid charge transfer at the electrode/electrolyte interface and the enhanced reaction kinetics of the electrode material. Moreover, the absence of a proper semicircle in the high-frequency region of the coated material denotes the negligible role of resistance caused by diffusion of

Na+ ions in the SEI layer. The introduction of Carbon into the material plays a critical role in improving the Na-ion diffusion of the carbon coated sample by altering the local structure of the cathode material. These results well agree with the excellent cycling stability exhibited by the carbon coated material in the limited cut-off voltage range.
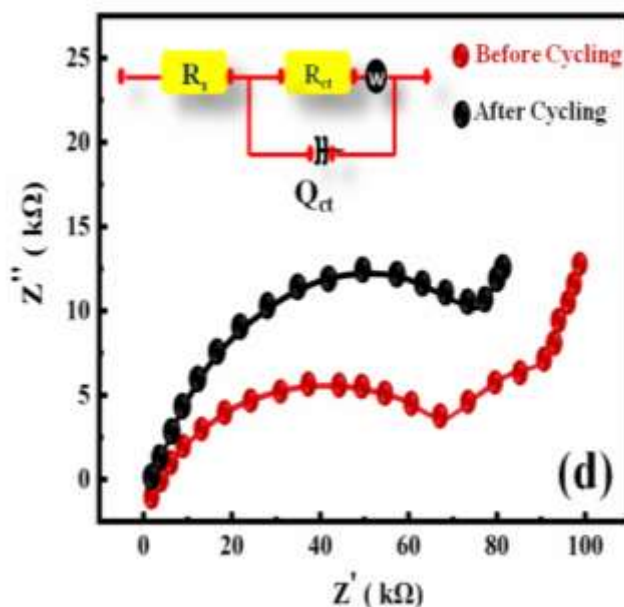


The carbon encapsulation over $NaFeO_2$ certainly hinders the unwanted sire reaction with electrolyte and subsequently prevents the formation of by-products in the form of SEI layer over the active material surface. This eventually facilitates the smooth transfer of ions and electrons over prolonged cycles [26]. Hence, these observations show the functional role of carbon coating in improving the electrochemical performance of layered oxides at high operating voltages. This work provides a new way of designing high-rate cathode materials for future SIB applications.

**VIII Conclusion.**

In this report we synthesis , Insitu carbon coated $NaFeO_2$ through gel assisted combustion method. The XRD results confirms the phase purity of the material and FESEM results clearly shows that the carbon was coated on the outer surface of the $NaFeO_2$ and it does not alter the nature of $NaFeO_2$. The electrochemical performance shows that the carbon coating greatly enhances the performance of the electrode materials. The cost effective and high stability electrode is suitable for large scale energy storage applications.

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