

Polymerized polyaniline (PANI) coated MnO₂ material enhanced performance of super capacitor electrical conductivity of the carbon

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Abstract

Super capacitor is an electrochemical energy storage device can charge and discharge very fast. Activated carbon is normally used as an electrode material for supercapacitor. The electrical conductivity of activated carbon is very low and cause ohmic loss and it ultimately hinders the charging capacities of the devices. In the present work an electrochemically deposited MnO₂ is employed to improve the electrical conductivity of the carbon. Moreover, the redox behavior of MnO₂ will contributes to the overall capacitance of the device. Prepared composite shows excellent capacitance of 230 F/g at 0.5 A/g current density. It is 1.8 times higher than Carbon alone. Similarly, the capacitance is lowering only 9% when the current density changes from 0.5 to 2 A/g. It indicates the better stability for the composite at higher current density. The calculated energy density and power density of the composite is 32.9 Wh/kg and 36.7 W/kg respectively, which is comparable and better than some of the recent reports. Current research activity opens a better path towards the improvement of charge storage properties of activated carbon.

Keywords: Activated carbon, PANI, Grafoil

1. Introduction

Electrochemistry is the branch of chemistry that deals with inter conversion of electrical energy and chemical energy [1]. It correlates the electrical energy and the chemical reactions which are redox reaction in nature. Substances which allow electric current to flow through them are called conductors [2]. Recent break through has made super capacitors a more viable and potentially safer charging option, but batteries still have advantages in cost and size. A capacitor is a passive two terminal electronic component that stores electrical energy in an electrical field. A capacitor can store electric energy when disconnected from its charging circuit, so it can be used like a temporary battery or like other types of rechargeable energy storage system[3-4]. A super capacitor is a high-capacity capacitor with capacitance values much higher than other capacitors that bridge the gap between electrolytic capacitors and rechargeable batteries. They typically can store 10 to 100 times more energy per unit volume or mass than electrolytic capacitors, can accept and deliver charge much faster than batteries, and tolerate many more charge and discharge cycles than rechargeable batteries[5-6].

Super capacitors do not use the conventional solid dielectric, but rather they use electrostatic double layer capacitance and electrochemical pseudo capacitance, both of which contribute to total capacitance of the capacitor[7-11]. Super capacitor can be divided into three types based on their charge storing mechanism.(Fig 1.) Therefore, 1. Double layer capacitor (Electrostatic), 2. Pseudo capacitor (Electrochemical) and 3. Hybrid capacitor (Both electrostatic & electrochemical capacitance)[12-13].

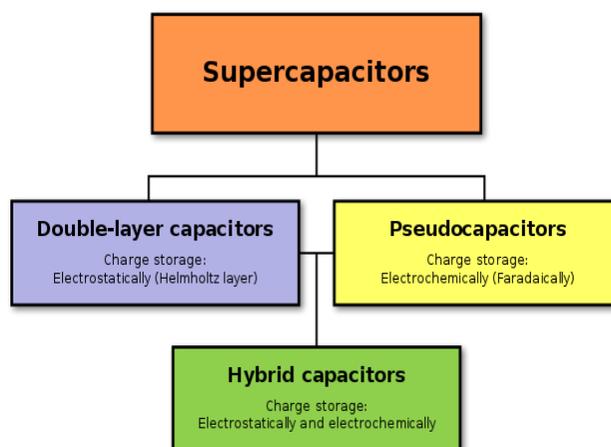


Figure1. Classification of electrochemical capacitor

Electrostatic double layer capacitor is used as a carbon electrode. It is followed the Helmholtz double layer mechanism. Pseudo capacitor is used as a conducting polymer electrodes & high amount of electrochemical process[14-16]. It is followed the faradaic electron charge transfer with redox reaction. Hybrid capacitor is both electrostatic & electrochemical capacitance. In this present paper represent the construction of super capacitor based on electrochemically polymerized polyaniline (PANI) and MnO₂ on activated carbon[17].

2. Experimental Methods

2.1 Chemicals:

PVDF –binder (Polyvinylidene formamide), NMP, Activated carbon, Grafoil sheet

2.2 Electrode fabrication

2.2.1 Preparation for carbon electrode

Weighed 26mg of PVDF and 50mg of Activated carbon. These two substance were added into motor and ground into paste by adding NMP(N-methyl pyrrolidone) drop by drop.

2.2.2 Coating of carbon slurry on carbon electrode:

Carbon electrode is prepared (7cm length and 1cm width) and weighed. The carbon slurry is coated on electrode in the dimension of 1cm length and 1cm width. Then electrode

was kept in the oven at 80°C and after 12 hours, taken out and cooled for 1 hour to get the coating of carbon on the electrode.

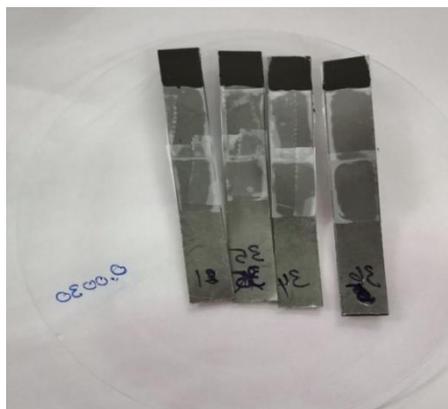


Figure 2 shown the carbon coated grafoil sheets

2.2.3 POLYMERISATION

2.2.3.1 Materials

Coated carbon strip, 0.5 M H₂SO₄, Aniline

Procedure

0.9 ml of aniline was dissolved in 49.1 ml of sulphuric acid and electrochemical polymerization performed using the 3 electrode system. Carbon coated grafoil sheet is the working electrode. Pt is a counter electrode and the SCE (Standard Calomel Electrode) is a reference electrode. Electrochemical deposition was performed at a current of 5 mA for 1 minute. After the polymerization electrode was cleaned using DI (Deionised) water and dried in the oven at 80°C. Then after drying, the weight of the deposited polymer was measured. The polymer coated carbon electrode is shown in fig 3.

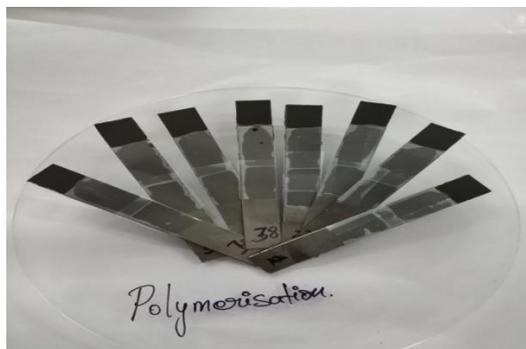


Figure 3. represent the polymer coated carbon electrode

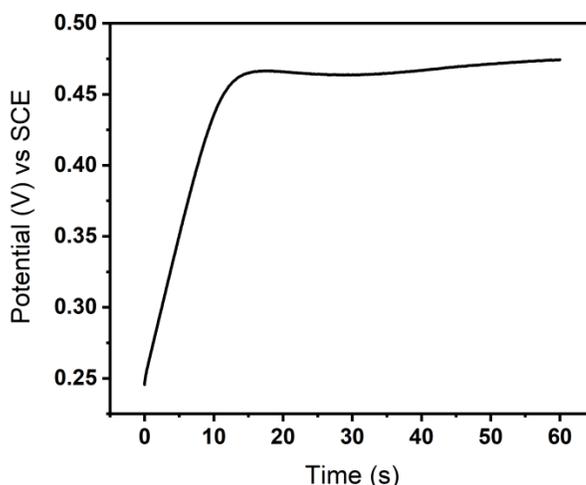


Figure 4 illustrate chronoamperometry profile for the electrochemical polymerization of aniline on carbon coated grafoil

2.2.3.4 Coating of MnO₂ on coated electrode

2.2.3.4.1 Materials

Manganese sulfate and Sodium sulfate

2.2.3.4.2 Procedure

(0.1M) 0.8451 g of manganese sulfate and (0.1M) 0.7102gm of sodium sulfate dissolved in Distilled water and Electrochemical decomposition performed using the 3 electrode system. Carbon coated grafoil sheet is the working electrode. Ptisa counter electrode and the SCE

(Standard Calomel Electrode) is are reference electrode. Experiment is carried out at constant potential vs SCE for 0.1Vs 10 minute. Carbon paper was dipped in ethanol before electrode position to enhance that hydrophilic nature. After the deposition of MnO_2 carbon strip is dried in the oven at 80°C and cooled. weighed the coated carbon strip deposited with MnO_2 (g).



Figure 5. Shows MnO_2 coated carbon electrode

2.3 SUPERCAPACITOR TESTING:

Two similar carbon electrode ((carbon (C) and polymer coated on carbon (C+ PANI) and MnO_2 coated on carbon) was used for the electrochemical studies. 0.5M sulphuric acid was used as electrolyte. Cyclic voltammogram was recorded at 5 mV/s scan rate and Charge discharge studies performed at different current densities such as 0.5 A/g, 1 A/g and 2 A/g. All the data were analyzed by using the EC-Lab software.

3. Results and Discussion

The polyaniline (PANI) coating was effectively done on the carbon coated grafoil by electro polymerization method[18-19]. A green color coating after polymerization on the carbon is clearly indicating the formation of polymer during the electro polymerization.

Further, cyclic voltammetry confirms the coating of PANI on the carbon (Figure 6). A well-defined redox peak observed during the CV for PANI coated carbon (C+PANI).

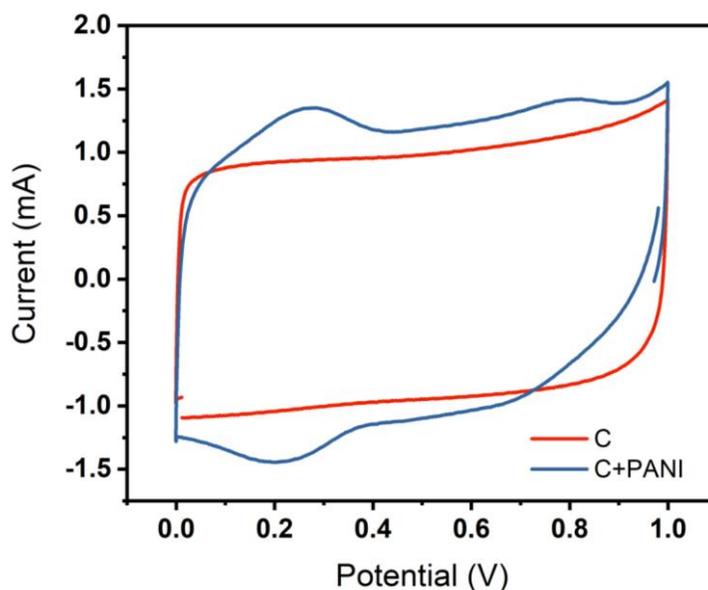


Figure 6. CV profile of carbon (C) and PANI coated Carbon (C+PANI) at a scan rate of 5 mV/s in 0.5 M H₂SO₄.

These redox couples are mainly arising from the oxidation and reduction reaction of PANI during higher positive and negative potentials. The carbon coated carbon strip shows perfect double layer capacitance behavior. The square type voltammogram of carbon indicates that there is no redox reaction on its surface.

The capacitance mainly arises from the adsorption of charges on the surface of the carbon. In the PANI coated carbon electrode, the capacitance is higher compared to carbon. The additional capacitance is arising from the redox behavior of the polymer.

The charge discharge profiles (Figure 7) of C and C+PANI further indicates the higher charge storage behavior of the composite. The calculated specific capacitance value from the slope of the discharge curve of C+PANI at 0.5 A/g is 230 F/g which is 1.8 times higher than carbon alone. The calculated specific capacitance from the slope of discharge curve of carbon is 130 F/g. The enhanced capacitance of C+PANI attributed the combined double layer charging

and pseudo capacitance arises from the polymer. Similarly, the conducting polymer improves the electrical conductivity of the activated carbon and reduces the ohmic resistance of the system. With increase in current density.

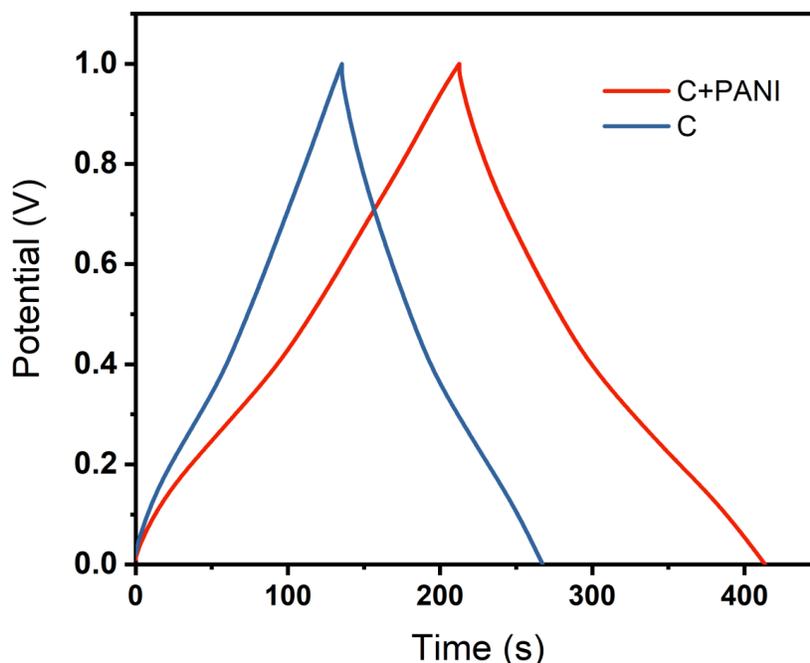


Figure 7. Charge-discharge profile of C and C+PANI at 0.5 A/g current density in 0.5 M H₂SO₄.

The specific capacitance of C+PANI is reducing (Figure 8). However, it shows only 9% reduction in performance at 2 A/g. But carbon alone shows a reduction in capacitance of 19%. This indicates that PANI coating on carbon improves specific capacitance as well as stability. The energy density and power density calculated for the C+PANI is 28.86 Wh/Kg and 29.4 W/kg respectively. These values are comparable to some of the reports.

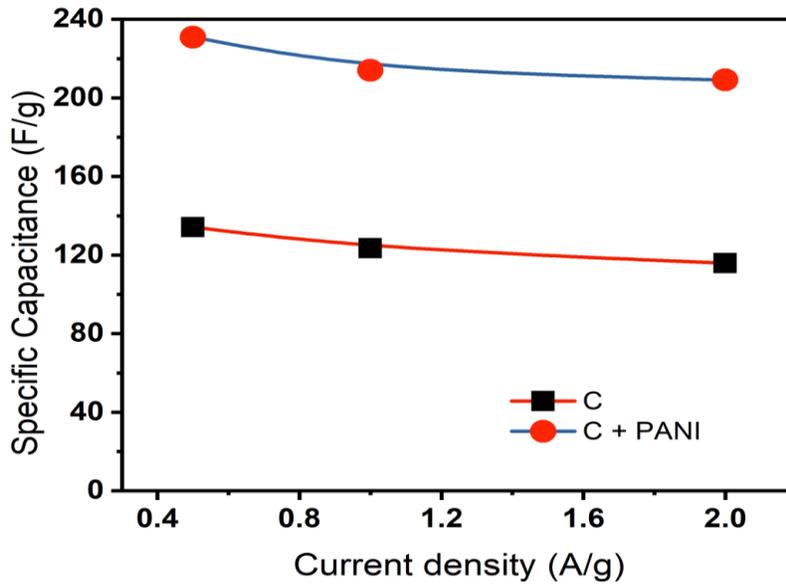


Figure 8. Specific capacitance of C and C+PANI at different current density measured in 0.5 M H₂SO₄.

The CV profile of carbon (C) and MnO₂ coated Carbon (C+ MnO₂) at a scan rate of 5 mV/s in 0.5 M H₂SO₄.

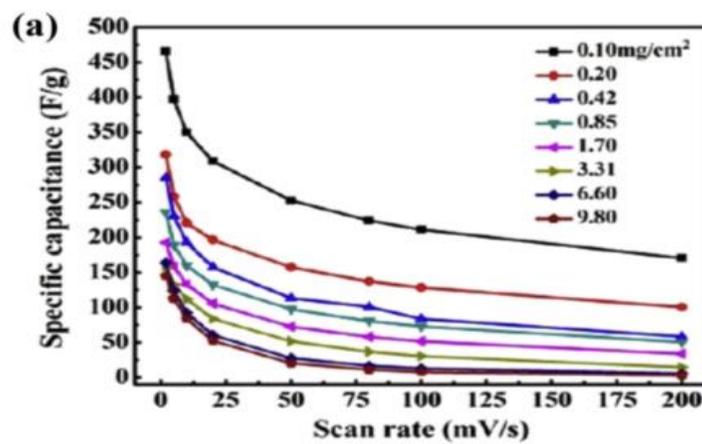


Figure 9. CV profile of carbon (C) and MnO₂ coated Carbon (C+ MnO₂) at a scan rate of 5 mV/s in 0.5 M H₂SO₄.

The Manganese dioxide (MnO₂) coating was effectively done on the carbon coated grafoil by electro deposition method. A green color coating after polymerization on the carbon

is clearly indicating the formation of polymer during the electro deposition[20-21]. Further, cyclic voltammetry confirms the coating of MnO₂ on the carbon (Figure 9). A well-defined redox peak observed during the CV for MnO₂ coated carbon (C+MnO₂). These redox couples are mainly arising from the oxidation and reduction reaction of MnO₂ during higher positive and negative potentials. The carbon coated carbon strip shows perfect double layer capacitance behavior. The square type voltammogram of carbon indicates that there is no redox reaction on its surface. The capacitance mainly arises from the adsorption of charges on the surface of the carbon. In the MnO₂ coated carbon electrode, the capacitance is higher compared to carbon. The additional capacitance is arising from the redox behavior of the polymer.

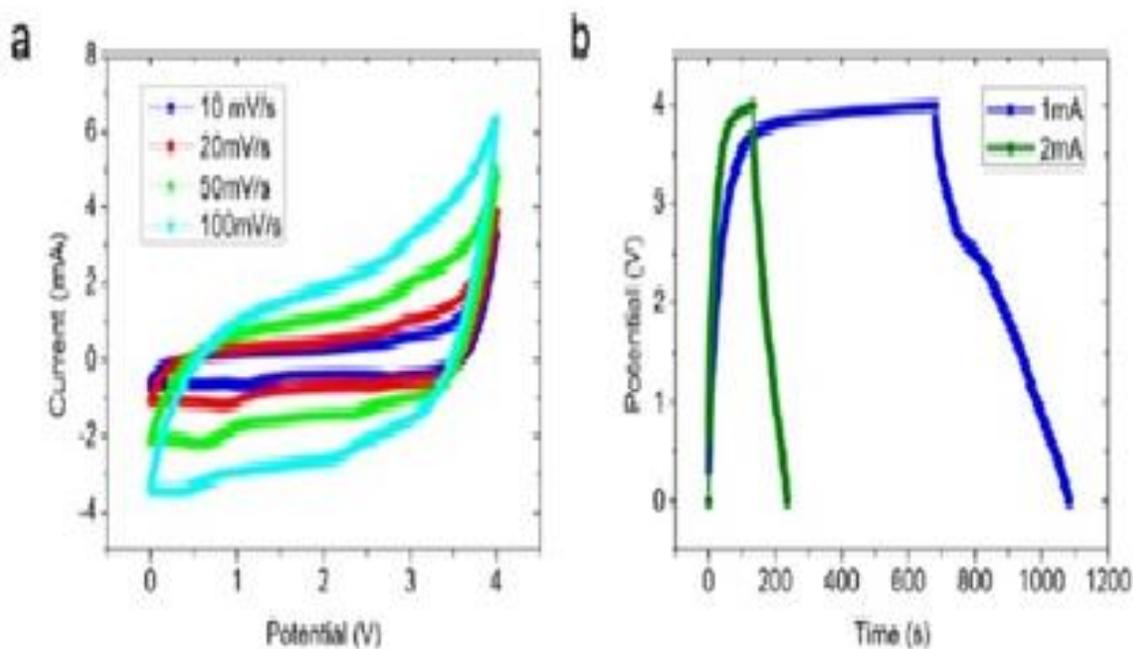


Figure 10. Charge-discharge profile of C and MnO₂ at 0.5 A/g current density in 0.5 M H₂SO₄.

The charge discharge profiles (Figure.10) of MnO₂ further indicates the higher charge storage behavior of the composite.

The calculated specific capacitance value from the slope of the discharge curve of MnO₂ at 0.5 A/g is 1149F/g which is 3.8 times higher than carbon alone. The calculated specific

capacitance from the slope of discharge curve of carbon is 230 F/g. The enhanced capacitance of MnO₂ attributed the combined double layer charging and pseudo capacitance arises from the deposition. Similarly, the MnO₂ improves the electrical conductivity of the activated carbon and reduces the ohmic resistance of the system. With increase in current density, the specific capacitance of MnO₂ is reducing (Figure 10). However, it shows only 5% reduction in performance at 2 A/g. But carbon alone shows a reduction in capacitance of 10%. This indicates that MnO₂ coating on carbon improves specific capacitance as well as stability. The energy density and power density calculated for the MnO₂ is 32.9 Wh/Kg and 36.7 W/kg respectively. These values are comparable to some of the reports.

S.No	Electrode	Energy density (Wh/Kg)	Power density (W/Kg)	Reference
1	PANI/NOMC	38.4	22	Synthesis and supercapacitor performance of polyaniline/nitrogen doped ordered mesoporous carbon composites
2	PANI and reduced graphene oxide (rGO) composite	25	20	Flexible supercapacitors based on polyaniline arrays coated graphene aerogel electrodes
3	GNS/CMWCNT/PANI	20.5	25	High performance asymmetric supercapacitor based on nano architecture polyaniline/graphene/carbon nanotube and activated graphene electrode
4	PANI/VA-CNTs	98.1	22.1	High performance supercapacitor based on electrochemical induced vertical aligned CNT and PANI nanocomposite electrode
5	C+PANI	28.8	29.4	Present work

6	AC+MnO ₂	5 - 10	19.3	Electrochemically grown nanoporous MnO ₂ nanowalls on a porous carbon substrate with enhanced capacitance through faster ionic and electrical mobility
7	Graphene + CNT	172	198	CO(OH) ₂ Nanosheet decorated graphene -CNT composite for supercapacitors of high energy density
8	Carbon + polyaniline			Effect of carbon porosity on the electrochemical properties of carbon/polyaniline super capacitor electrodes
9	TiO ₂ + C + MnO ₂	46.8	22.4	Construction of TiO ₂ Nanotubes/C/ MnO ₂ composites films as a binder free electrodes for a high performance supercapacitor
10	MnO ₂	33.8	32.9	Research progress in MnO ₂ -Carbon based supercapacitor electrode materials
11	C + MnO ₂	32.9	36.7	Present work

4. Conclusion

The present study deals with the construction of supercapacitor based on electrochemically polymerized polyaniline on activated carbon. The experimental methods employed in the coating of PANI on carbon electrode used for simple electrochemical polymerization technique. The results obtained illustrate that Polyaniline effectively coated on activated carbon. The redox peak for C+PANI in the cyclic voltammogram indicates the effective coating of PANI on carbon. C+PANI display a specific capacitance of 230 F/g at 0.5 A/g current density which is 1.8 times higher than the specific capacitance of the carbon at the same current density. The energy density and power density of the C+PANI is 28.86 Wh/Kg and 29.4 W/Kg respectively. MnO₂ is effectively coated on activated carbon by a simple electrochemical technique. The redox peak for MnO₂ in

the cyclic voltammogram indicates the effective coating of C+PANI on carbon. MnO_2 display a specific capacitance of 1149 F/g at 0.5 A/g current density which is higher than the specific capacitance of the carbon at the same current density. The energy density and power density of the MnO_2 is 32.9 Wh/Kg and 36.7 W/Kg respectively. The obtained results shows an effective method to improve the capacitance and electrical conductivity of the carbon by a simple polymer coating and MnO_2 technique.

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References

1. S. Sarangapani, B.V. Tilak, and C.P. Chen, J. Electrochem. Soc, 1996, 143, 3791-3799.
2. C. Arbizzani, M. Mastragostino, and B. Scosati, Nalwa, Wiley, Chichester, UK, 1997, 4.
3. B.E. Conway, Kluwer Academic/Plenum, New York, USA, 1999.
4. K. Babel, K. Jurewicz, J. Phys. Chem. Solids, 2004, 65(2-3), 275-280.
5. M.M. Ishak, M.Deraman, I.A. Talib, N.H. Badri, Awitdrus, R.Farma, R.Omar, N.S.M. Nor and B.N.M. Dolah. AIP Conference Proceeding, 2015, 1656, 030005
6. Li Bai, Xingyan Wang, Xianyou Wang, Xiaoyan Zhang, Wanmei Long, Hong Wang, and Xiaoshuan Li, J. Power sources, 2010 195, 1747-1752.
7. Elzbieta Frackowiak, Phys.Chem.Chem.Phys, 2007,9,1774-1785.
8. Wei Xing, Shuping Zhuo, Hongyou Cui, Weijiang Si, Xiuli Gao, Zifeng Yan, J porous mater, 2008, 15,647-651.
9. H.Krawiec, V.Vignal, O.Heintz, R.Oltra, Electrochimica Acta, 2006, 51(16), 3235-3243..
10. Yjming Chem, Lijie Ahou, Jing Wei, Changton Mei, Shaohua Jiang, Mingzhu Pan, Changyan Xu,. Journal of electronic materials, 2019, 48 (5), 3157-3168.
11. Q.F. Xiao, X. Zhou, Electrochim. Acta, 2003, 48(5), 575-580 .
12. Ahanxin Xiong, Ru Wang, Shuaishuai Li, Bohua Wu, Jia Chu, Xiaoqin Wang, Runian Zhang,Ming Gong, Journal of electronic materials, 2018, 47(7), 3974-3982.

13. E. Frackowiak, V. Khomenko, K. Jurewicz, K. Lota, F. Beguin, J. Power Sources, 2006, 153(2), 413-418.
14. Xinzhen Wang, SongQiu, Guixia Lu, Cuizhu He, Jiurong Liu, Ligiang Iuan, Weil Liu, CrystEngComm, 2014,16, 1802-1809.
15. Muthu Selvakumar, and Sethuraman Pitchumani,. Korean J.Chem.Eng, 2010, 27(3),977-982.
16. Prathamesh P.Deshpande, Meera Murali, Pravin P. Deshpande, Vidyanand S. Galphade, Mahendra A, Chemical papers, 2013, 67 (8), 1066-1071.
17. Hua Fang, GaoyunChen, Lixia Wang, JiYan, Linsen Zhang, KezhengGao, Yongxia Zhang, Lizhen Wang, RSC Adv., 2018, 8, 38550-38555..
18. Suniya Shahzad, Afzal Shah, Elaheh Kowsari, Faiza Jan Lftikhar, Anum Nawab, Benoit Piro, Mohammad Salim Akhter Usman Ali Rana Youqjjn Zou,Global Challenges 2019,3,1800023.
19. Seyed Abbas Rahim, Parviz Norouzi, Mohammad Reza Ganjali, RSC adv, 2018, 826818-26827.
20. Banafsheh Babakhani, Douglas G.Ivey, J Power sources, 2010, 195(7), 2110-2117.
21. Tian Yi Ma, Sheng Dai, Mietek Jaroniec, Shi Zhang Qiao, Journal of the American Chemical Society, 2014, 136 (39), 13925-13931.