Synthesis, characterization and DC conductivity of Polyaniline/Manganese dioxide composites.

Sweta M Nayak[1], Jakeer Husain[2], Sangshetty Kalyane[3], M.V.N. Ambika Prasad[1*]
[1]Department of Studies and Research in Physics, Gulbarga University, Kalaburgi-585105, India
[2]Department of Engineering Physics, KBN college of Engineering, Kalaburagi, Karnataka, India
[3]Department of Physics, BKIT Bhalki, Bidar , Karnataka , India

ABSTRACT: - Polyaniline composites using metal oxides have wide variety of applicability because of its enhanced properties to that of pure polyaniline. Here, manganese dioxide is employed as the metal oxide to synthesize Polyaniline composite (PANI-MnO_2) through in-situ chemical oxidative polymerization. The obtained PANI-MnO_2 is characterized for X-Ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM). DC conductivity was studied in the temperature range from 30–180^{0}C. It is observed that conductivity remains constant up to 100^{0}C and then increases exponentially.

Keywords:- Conducting polymer, XRD, FTIR, SEM, Polyaniline, Chemical oxidative polymerization.

1. Introduction:-

The discoveries of conducting polymers have opened up a new promising field in materials science and engineering. Among them, conducting polyaniline (PANI) is one of the most promising conducting polymer because of its unique electrical, optical and opto-electrical properties, as well as its ease of preparation and excellent environmental stability. Polyaniline can be used in electrochromic device, light-emitting diodes, electrostatic discharge protection, secondary batteries etc (1-4). Conducting polymers have shown much higher specific capacita- nce and the cost is low (5-9). Polyaniline (PANI) (10), polypyrrole (11-12), polythiophene (13), and so forth, have been investigated widely. Researches on the synthesis, structure, properties, and applications about polyaniline have been explored and developed greatly in the past few years (14-17). MnO_2 is one kind of widely studied transition metal oxides, which is cheap, available in abundance, and environmentally friendly (18-21).

2. Experimental:-

Materials and methods:-

All the reagents were analytical grade only and were used as received. Aniline monomer was distilled under reduced pressure and kept below 0-5 ^{0}C prior to use. Aniline monomer, hydrochloric acid (HCl), ammonium per sulphate [$(NH_4)_2S_2O_8$] and manganese dioxide (MnO_2) were purchased from s.d. fine chemicals ltd i.e., SDFCL MUMBAI.

2.1. Synthesis of Polyaniline (PANI):-

Synthesis 0f PANI was carried out by in-situ chemical oxidation polymerization Technique. Aniline (0.1M) was mixed in 1M hydrochloric acid and stirred for 15 min to form aniline hydrochloride. To this solution, add 0.1M of ammonium persulphate, which acts as an oxidizer was slowly added drop-wise with continuous stirring at 0-5^{0}C for 4 hrs to get it completely polymerized. The precipitate was filtered, washed with deionized water, acetone and finally dried in an oven at 60^{0}C for 24hrs to achieve a constant mass. In this way, polyaniline (PANI) is synthesized.

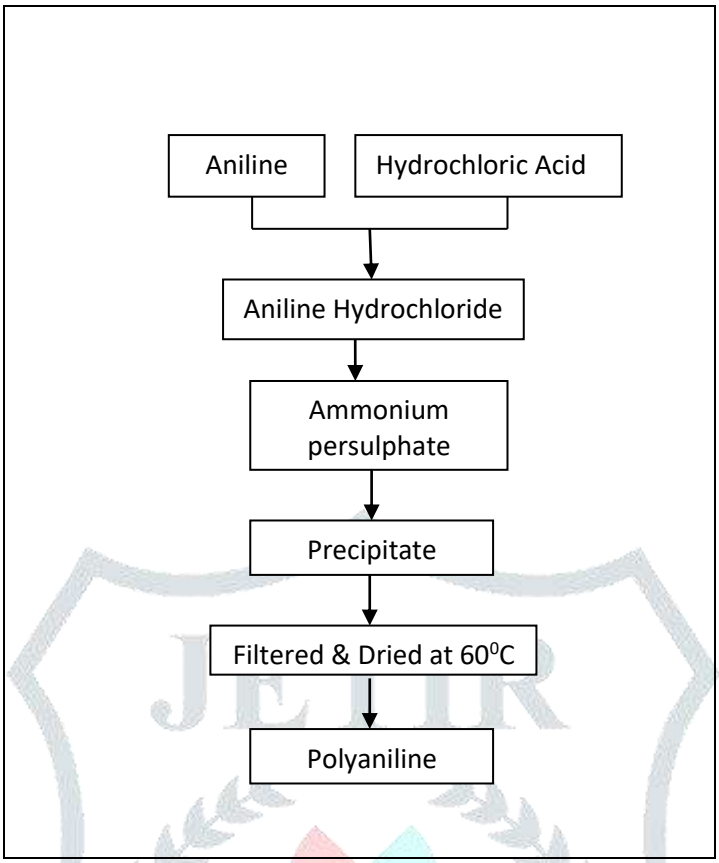

Fig-1a:- Flow chart of Pure Polyaniline

2.2. Synthesis of PANI/MnO_2 composites:-

Synthesis of PANI/MnO_2 composites was carried out by In-situ chemical oxidation polymerization technique. Aniline (0.1M) was mixed in 1M hydrochloric acid and stirred for 15 min to form Aniline hydrochloride. MnO_2 powder is added in the mass fraction to the above solution with vigorous stirring in order to keep the MnO_2 homogeneously suspended in the solution. To this solution, add 0.1M of ammonium persulphate, which acts as an oxidizer was slowly added drop-wise with continuous stirring at 0-5^{0}C for 4 hrs to be completely polymerized. The precipitate was filtered, washed with deionized water, acetone and finally dried in an oven for 24hrs to achieve a constant mass. In this way, polyaniline/MnO_2 composites with various weight percentages of MnO_2 (10%, 20%, 30%, 40% and 50%) were synthesized. Later, the synthesized samples were made a fine powder with the help of agate mortar.

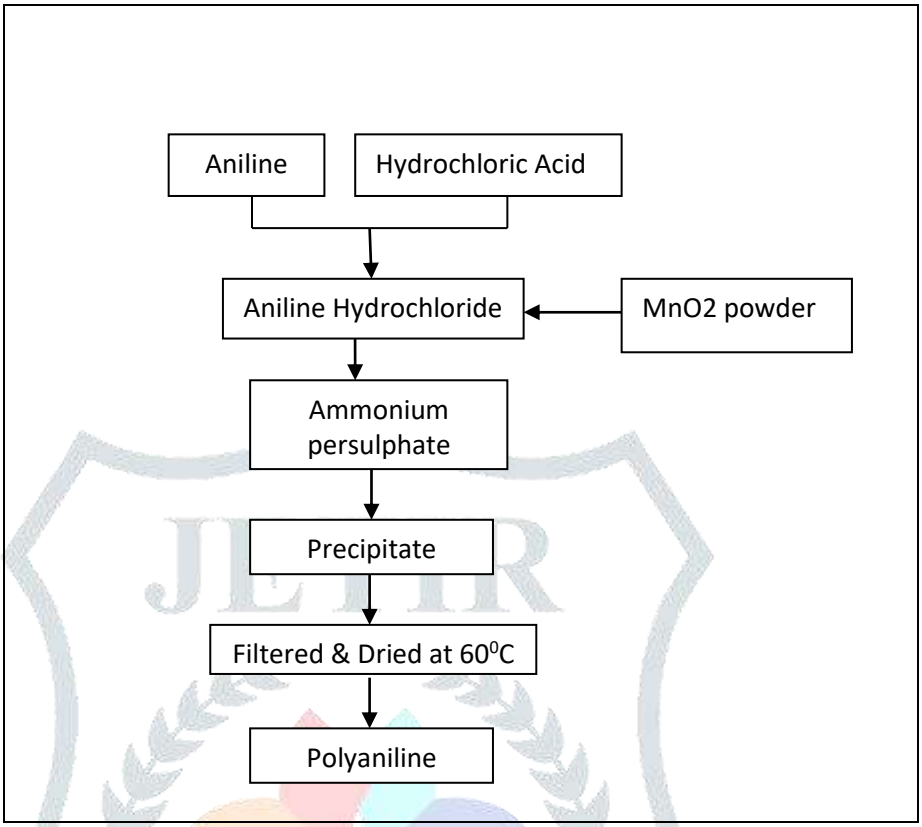

Fig- 1b:-Flow chart of Polyaniline/manganese dioxide composite

2.3. Characterization:-

X-Ray diffraction studies were performed using Philips X-ray diffractometer with CuK_α as the radiation source. Fourier transform infrared spectra were recorded on thermo Fisher ATR Nicolet model using diamond (iS5) in the range 4000-400cm^{-1}. The morphology of the composites in the form of powder were investigated using scanning electron microscope (SEM) Model-EVO-18 (Special Edison, Zeiss, Germany). The DC conductivity of PANI and PANI/TiO_2 composites were studied by using Keithley 6514 Electrometer. For DC conductivity studies, the samples were prepared in the pellet form (10 mm diameter and thickness varying up to 2 mm) by applying pressure of 10 tons in a Universal testing machine. The pellets were coated with silver paste on either sides. Temperature dependent electrical conductivity was measured from 30^{0}C to180^{0}C using Keithley 6514 electrometer.

3. Results and Discussions:-

3.1. XRD analysis:-

Figure 2(a-c) shows X-ray diffraction pattern of Polyaniline, Pure manganese dioxide (MnO_2) and PANI/MnO_2 composites respectively. The analysis of X-ray diffraction of Polyaniline suggests that it has amorphous structure with a broad peak centered on $2\theta \approx 25^0$. Figure 2b shows the X-ray diffraction pattern of pure manganese dioxide (MnO_2) composite shows well defined broad peaks, which indicates good crystallinity of the materials. The observed 2theta values are consistent with the standard JCPDS no-80-1098. Figure 2c shows X-ray diffraction pattern of Polyaniline – MnO_2 composite. The resulting diffractogram shows a perfect crystalline structure which may be due to the presence of MnO_2. The

comparison of XRD pattern of MnO_2 and composite suggests that there is no change in the structure of MnO_2 which is due to its dispersion in polyaniline during polymerization reaction.

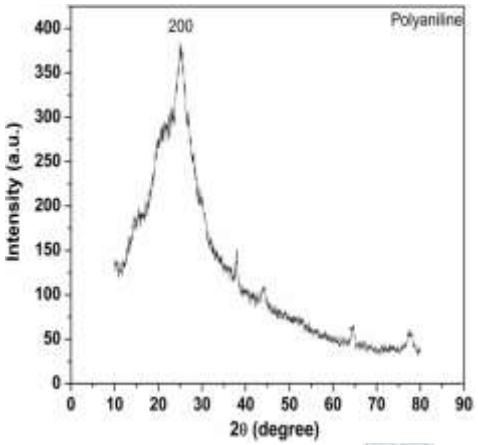

Fig-2a:- XRD of Pure polyaniline

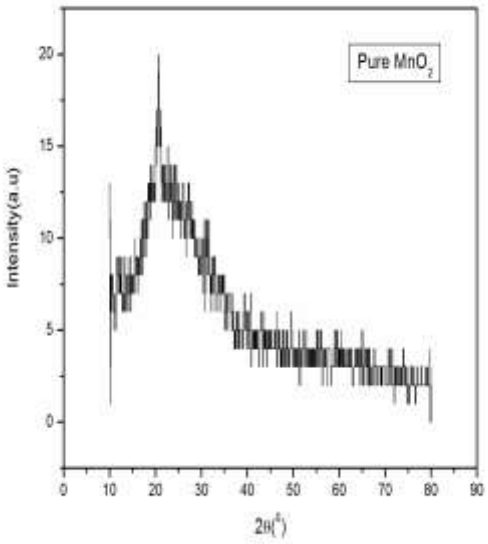

Fig-(2b):- XRD of Pure MnO2.

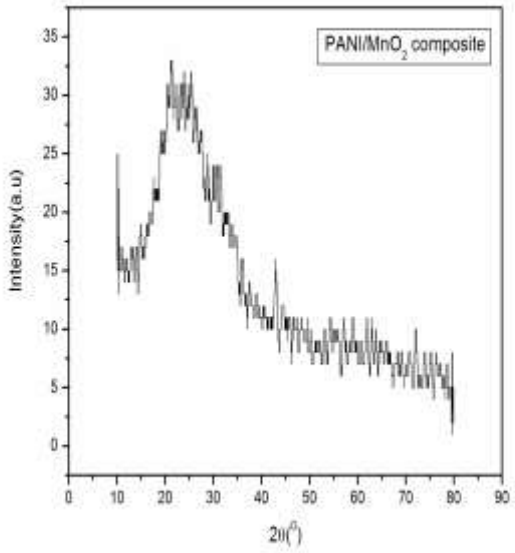

Fig-(2c):- XRD of PANI/MnO_2 composite

3.2. FTIR analysis:-

Fig-3a shows IR spectra of pure Polyaniline where the percentage transmittance is plotted as a function of wave number in cm^{-1}. IR spectra reveals the presence of intensity peaks at 3400, 2900, 2800, 1700, 1500, 1000, 700, 550 cm^{-1}. The intensity peaks at 1500, 1000 and 700 may be attributed due to the presence of C = N, N – H and C – N stretching frequencies. The occurrence of various bands in IR spectra may be attributed due to the following factors.

Sample	Mode of vibration	Peak position (cm^{-1})
Pure Pani	C=N stretching	1500
	N-H stretching	1000
	C-N stretching	700

Fig-3b shows that the spectra of Pure MnO_2 that has predominant peaks at the wave number of 3431cm^{-1} which is due to O-H vibration and is formed at higher frequency due to splitting of water molecules on the surface of MnO_2 particles, the peak at 2900cm^{-1} is due to the N-H stretching, the peaks at 1601 to 1490cm^{-1} is due to C-H in plane bending modes and the peaks at 657cm^{-1} corresponds to metallic stretch that can be assigned to MnO_2 group.

Sample	Mode of vibration	Peak position (cm^{-1})
Pure MnO_2	O-H stretch	3431
	N-H stretch	2900
	C-H bending	1601 to 1490
	Metallic stretching	657

Fig-3c shows the spectra of PANI/MnO_2 composite a large broad bands appears at 3434cm^{-1} which is due to the O-H stretch because of the absorption of water molecules, the peaks at 1793 and 1684cm^{-1} is due to C=O aromatic stretch, the peaks at 1560 and 1451$cm^{-1}$is due to the C-H stretch , the peaks from 960cm^{-1} is due to alkene=C-H bending and peaks from 625cm^{-1} is due to the metallic stretch.
The characteristic stretching frequencies are shifted toward higher frequency side indicates that homogeneous distribution of MnO_2 particle in the polymeric chain. This may be attributed due to the Vander walls force of attraction between MnO_2 and polymeric chain.

Sample	Mode of vibration	Peak Position(cm^{-1})
PANI/ MnO_2 composite	O-H Stretch	3434
	C=O stretch	1793&1684
	C=H bending	1560 to 1451
	Alkene=C-H bending	960
	metallic stretch	625

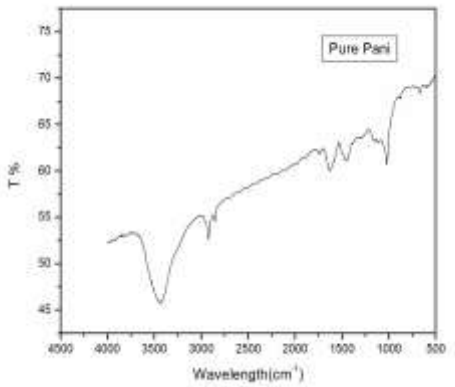

Fig- 3a:-FTIR of Pure Polyaniline

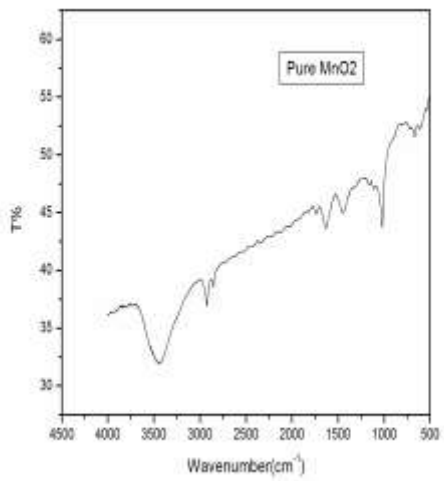

Fig-3b:- FTIR of pure MnO_2

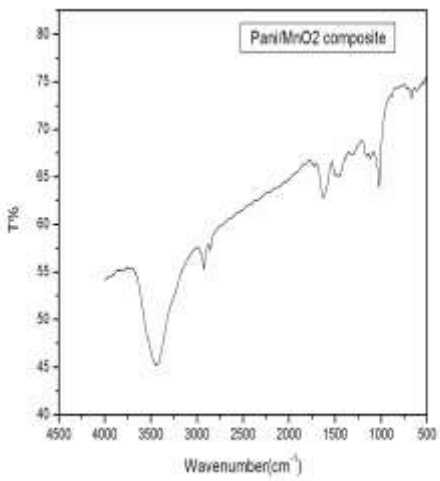

Fig-3c:- FTIR of PANI/ MnO_2 composite

3.3.SEM analysis :-

Figure-4a shows the SEM micrograph of conducting Polyaniline It is seen clearly from the SEM micrograph of Polyaniline that, it has a clusters of spherical shaped particles with elongated chain pattern. Figure-4b and 4c shows the scanning electron micrograph of pure MnO_2 and Polyaniline – MnO_2 composite respectively. Fig-4b of pure MnO_2 shows that the particles are highly mesoporous, agglomerated granular in shape and the particles are well interconnected to each other.

A very high magnification reveals the presence of MnO_2, which is spherical in shape, homogeneously distributed throughout the polymer sample absorbed in fig 4c. The presence of such sharp crystals of MnO_2 has a strong influence on various electrical parameters such as conductivity and dielectric behavior of these composites. The contrast in the images is due to the differences in scattering from different surface areas as a result of geometrical differences between Polyaniline and MnO_2.

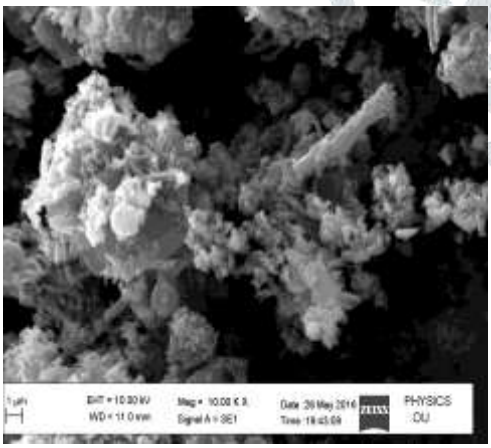

Fig-4a:- SEM images of pure polyaniline

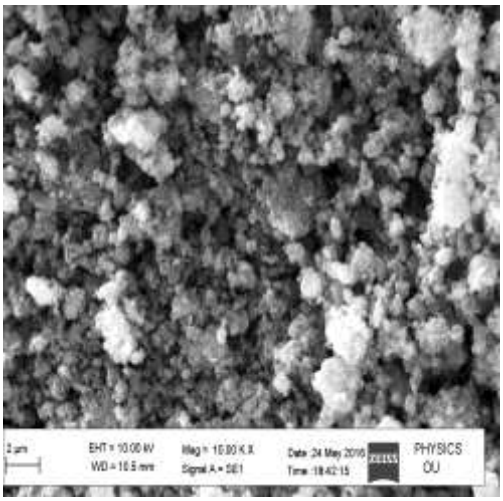

Fig-4b:- SEM image of Pure MnO_2

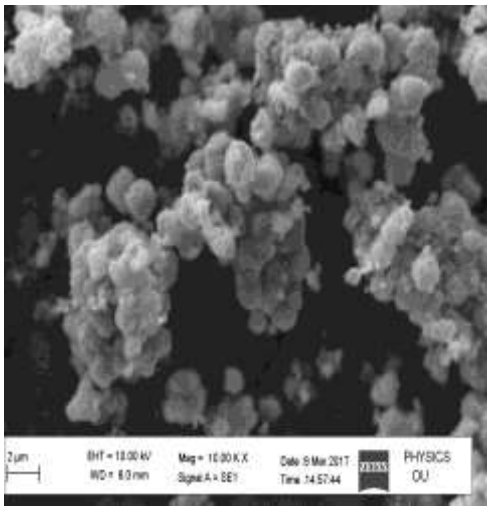

Fig-4c:- SEM image of PANI/MnO_2 composite

3.4. DC Conductivity: - Figure-5 shows the variation of dc conductivity as a function of temperature. It is observed that the value of dc conductivity of these composites increases exponentially with temperature. It remains nearly constant up to 80^0C and there after it increases exponentially. The conductivity behavior is the characteristic of amorphous materials. The initial increase in the values of conductivity is due to the extended chain length of Polyaniline due to which the hopping charge carriers occurs between the favorable localized sites, further it is also observed that the conductivity increases with the increases of wt% of MnO_2 in PANI is due to the variation in distribution of MnO_2 particles in PANI. The composite having 30wt% of Pani/MnO_2 shows the highest conductivity than pure PANI.

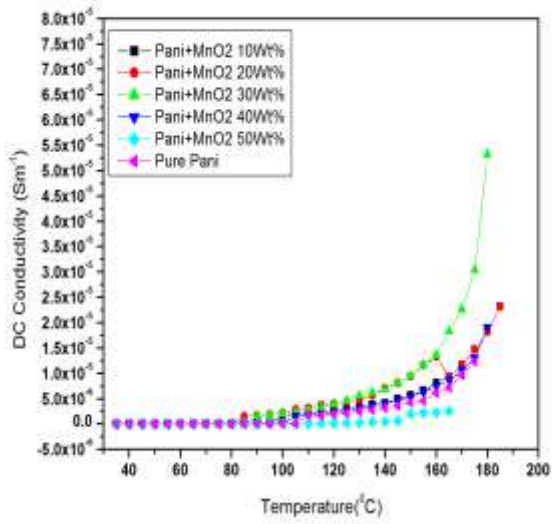

Fig-5:-DC conductivity of PANI/MnO2 composite

IV. Conclusion:-

Polyaniline/MnO_2 composites were synthesized by in-situ polymerization method. The prepared composites were characterized by XRD, FTIR, SEM, and their results were confirmed by the formation of composite and indicate an interaction between PANI and manganese dioxide particles. In case of DC conductivity, it is observed that the conductivity increases with the increase in the concentration of Titanium dioxide particles.

References:-

1. Gospodinova, N.; Terlemezyan, L. Prog Polym Sci ., 23, 1443(1998).
2. MacDiarmid, A. G. Angew Chem Int Ed., 40, 2581(2001).
3. Huang, J. X.; Virji, S.; Weiller, B. H.; Kaner, R. B. J Am ChemSoc., 125, 314(2003).
4. Virji, S.; Huang, J. X.; Kaner, R. B.; Weiller, B. H. Nano Lett., 4, 491(2004).
5. Y. Sun, S.R. Wilson, and D.I. Schuster, J. Am. Chem. Soc.,123, 5348 (2001).
6. V. Khomenko, E. Frackowiak, and F. Beguin, Electrochim. Acta, 50, 2499 (2005).
7. Y.K. Zhou, B.L. He, W.J. Zhou, J. Huang, X.H. Li, B. Wu, and H.L. Li, Electrochim. Acta, 49, 257 (2004).
8.Y.K. Zhou, B.L. He, W.J. Zhou, and H.L. Li, J. Electrochem.Soc., 151, A1052 (2004).
9. K.R. Prasad and N. Munichandraiah, J. Power Sources, 112,443 (2002).
10. T.C. Girija and M.V. Sangaranarayanan, Synth. Met., 156,244 (2006).
11. X.M. He, C. Li, F.E. Chen, and G.Q. Shi, Adv. Funct. Mater., 15, 2911 (2007).
12. D.T. Henry, S. Koo, G.H. Won, M.D. Julio, W.K. Robert, H.W. Bruce, and B.K. Richard, Macromol Rapid Commun., 28, 2289 (2007).
13. X.G. Li, J. Li, Q.K. Meng, and M.R. Huang, J. Phys. Chem. B, 113, 9718 (2009).
14. D.Y. Kim, H.N. Cho, and C.Y. Kim, Progr. Polym. Sci., 25,1089 (2000).
15. A. Pron and P. Rannou, Progr. Polym. Sci., 27, 135 (2002).
16. X.G. Li, A. Li, and M.R. Huang, Chem. Eur. J., 14, 10309(2008).
17. X.G. Li, Q.F. Lu, and M.R. Huang, Small, 4, 1201 (2008).
18. M. Xu, L. Kong, W. Zhou, and H. Li, J. Phys. Chem. C,111, 19141 (2007).
19. S. Devaraj and N. Munichandraiah, J. Phys. Chem. C, 112, 4406 (2008).
20. M. Toupin, T. Brousse, and D. Belanger, Chem. Mater., 14, 3946 (2002).
21. Q. Li, J.B. Olson, and R.M. Penner, Chem. Mater., 16, 3402 (2004).