

Electrical Characterization of (70PEO:30AgNO₃)_(1-x)(TiO₂)_x Nanocomposite Polymer Electrolyte for Energy Storage Devices used in HEV

Manish Kurrey^{1*}, Satpreet Singh Gill², Nirbhay K Singh^{3*}, Ggandeeep Singh Gill⁴, O. P. Verma⁵

^{1,2}Dept. of Electrical Engineering, Kalniga University, Raipur (C.G.), India

³Dept. of Applied Physics, Krishna Engineering College, Junwani, Durg (Chhattisgarh), India

⁴Dept. of Mechanical Engineering, Kalniga University, Raipur (C.G.), India

⁵Dept. of Electronic and Telecommunication Engineering, ISBM University, Gariyaband (C.G.), India

Corresponding Author: sajangill017@gmail.com

DOI: <https://doi.org/10.26438/ijcse/v7i5.932936> | Available online at: www.ijcseonline.org

Accepted: 20/May/2019, Published: 31/May/2019

Abstract— Poly (ethylene oxide) (PEO) based Nano-Composite Polymer Electrolyte (NPE) membranes (70PEO:30AgNO₃)_(100-x)(TiO₂)_x, where $x = 0 \leq x \leq 10$ wt% have been casted by hot-press/solution free technique. Solid Polymer Electrolyte (SPE) composition 70PEO:30AgNO₃ (wt. %), has highest conducting film with room temperature conductivity $\sigma_{\pi} \sim 3.6 \times 10^{-6} \text{ Scm}^{-1}$, has been used as the first phase host matrix and TiO₂ filler particles of nano-dimension (< 100 nm) as second phase dispersion. The fractional dispersal of TiO₂ filler (viz. $x = 3$ wt. %) in SPE host results increase in room temperature conductivity. This NPE film (70PEO:30AgNO₃)₉₇(TiO₂)₃ referred as Optimum Conducting Composition NPE(OCC) film. The morphological analysis performed by Scanning Electron Microscopy (SEM) techniques. The ionic transport properties characterized by basic ionic parameters viz. conductivity (σ), mobility(μ), mobile ion concentration (n), ionic transference number (t_{ion}) and cationic transport number (t_{+}). Using these electrolytes a thin symmetric capacitor has been prepared which shows capacitance about 5 F/g of in the cycling in the range of 0–1.5 V at 0.5 A g⁻¹.

Keywords—Solid polymer electrolyte, Energy Storage devices, Supercapacitor, Hybrid electric Vehicle.

I. INTRODUCTION

Polymer electrolytes are extensively used in all-solid-state electrochemical power sources viz. batteries, fuel cells, supercapacitors etc. . The first ion conducting solid polymer electrolyte based battery was reported in 1973 and 1979 respectively [1, 2]. Since then, wide variety of SPE materials, involving different mobile ionic species have been investigated [3-20]. Poly (ethylene oxide) PEO shows higher stability, dissolve wide variety of salts as compare to other polymers having polar and flexible main chain. These ions can migrate through the amorphous region of the polymer via inter/intra chain segmental motion. It exhibit low ionic conductivity at room temperature but it can be significantly increased by fractional dispersal of nano size inert filler particles such as Al₂O₃, SiO₂, TiO₂ etc [9-20]. Present work report physical and electrochemical properties of NPE membranes (70PEO:30AgNO₃)_(1-x)(TiO₂)_x casted by hot press method. SPE film composition: 70PEO:30AgNO₃, [21] having highest ionic conductivity at room temperature, has been used as first phase host matrix and nano-particles (< 100 nm) of TiO₂ as second phase dispersoid. The composition (70PEO:30AgNO₃)₉₇(TiO₂)₃ identified as highest conducting film, their physical properties characterized by SEM, EDS and TGA techniques,

the electrochemical properties has been studied in terms of basic ionic parameters viz. conductivity (σ), activation energy (E_a), mobility (μ), mobile ion concentration (n), ionic transference number (t_{ion}) and ionic transport number (t_{+}). A new class of solid state capacitors consisting of (70PEO:30AgNO₃)₇₀(AC)₃₀ as electrode designated [22, 23] and synthesized NPE (OCC) as electrolyte is presented, and the results are discussed.

II. EXPERIMENTAL

Hot press method is used for the preparation of electrode and electrolyte using AR grade chemicals: poly (ethylene oxide) (PEO) (Mw ~ 6x10⁵, Aldrich, USA), AgNO₃ (purity ~ 99.9%, Reidel, India), TiO₂ (size < 100nm, Aldrich, USA), AC powder (surface area 14s00 m²/g, pore volume is 0.45 cm³/g). The earlier reported standard electrolyte (70PEO:30AgNO₃) was used as the base material. Conductivity (σ) measurements have been carried out using LCR meter [HIOKI 3522-50, Japan] in the frequency range 50 Hz to 5 MHz. The activation energy E_a calculated by Arraheneous plot at different temperature and composition. Ionic mobility (μ), carrier ion concentration (n) and ionic transference number (t_{ion}) of NPE (OCC) measured by a dc polarization Transient Ionic Current (TIC) technique [24]

using x-y-t recorder (Graphtec WX – 2300). In order to separate out the cationic (Ag^+) transport number, a combined ac/dc technique, is used [25]. Surface morphology and EDS analysis performed with the help of SEM (JEOL-JSI microscope) fitted with EDS. The electrolyte is sandwich between PAC electrode by gradually increasing pressure about 2-tone to make the contact between electrode and electrolyte. The performance of capacitor analyse by using leakage and discharge current profile and Cyclic Voltammetry.

III. RESULTS & DISCUSSION

The Impedance plot for NPE shows a semicircular arc which intercept on real axis, corresponds to blocking impedance R_b (figure 1). The conductivity of composition calculated by

$$\sigma = \frac{t}{R_b A}$$

where area $A \sim 1.85 \text{ cm}^2$, and the

results are shown in figure 2. The conductivity maxima $\sigma_{max} \sim 2.35 \times 10^{-5} \text{ S/cm}$ were obtained at $x = 3$ of TiO_2 in SPE it referred as optimum conducting composition NPE(OCC), it is due to the dissociation of ion aggregates and/or undissociated salt which resulted into the generation of free ion carriers as a consequence of addition of nano-sized TiO_2 . But larger amount of filler create non conducting path which results decrease in conductivity. The activation energy of each composition calculated by Arrhenius plot shown in figure 2, it indicate that lowest activation energy corresponds to OCC found to be 0.22eV.

The Ionic parameters (μ , n) and total ionic transference number (t_{ion}) of optimum conducting film have also been determined by TIC technique. The experimental arrangement of which is shown in figure 3(a), μ has been measured at different temperatures below T_m with help by equation $\mu = d^2 / V \tau$, where d and τ stands for thickness of sample and transient time respectively and V is applied dc potential, n is number of charge carrier given by equation $n = \sigma / \mu . q$.

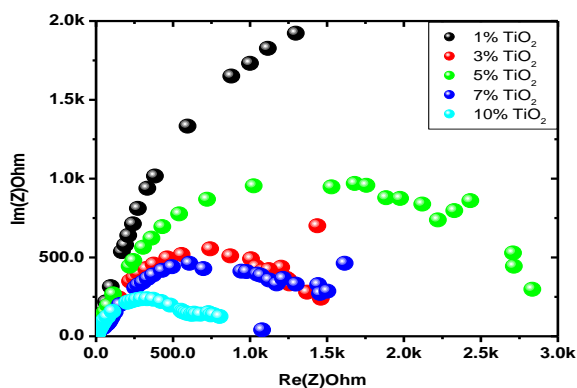


Figure 1: Cole-Cole plot for $(70PEO:30AgNO_3)_{(1-x)}(TiO_2)_x$

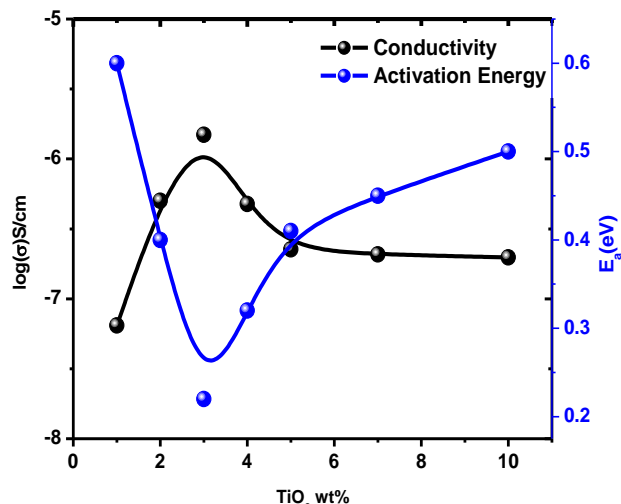
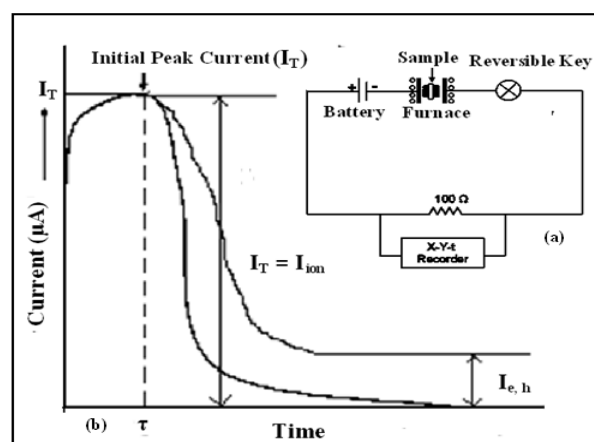


Figure 2: Conductivity and Activation energy plot for NP

The plot between $\log \mu - 1/T$ and $\log n - 1/T$ for NCP(OCC) shown in Figure 3(b), which reveals that μ almost remain unaltered with the decrease in temperature and n increased with increasing temperature because of more carrier ions generation. The total ionic transport number (t_{ion}) can also be determined from current – time TIC plot shown in Figure 3(c) using equation $t_{ion} = 1 - (I_{e,h} / I_T)$. The total current approached close to zero in about 2 hrs indicating that the mobile ions in the cell SS //NPE(OCC)// SS, subjected to an external dc potential, have been completely polarised at the respective electrode / electrolyte interfaces.



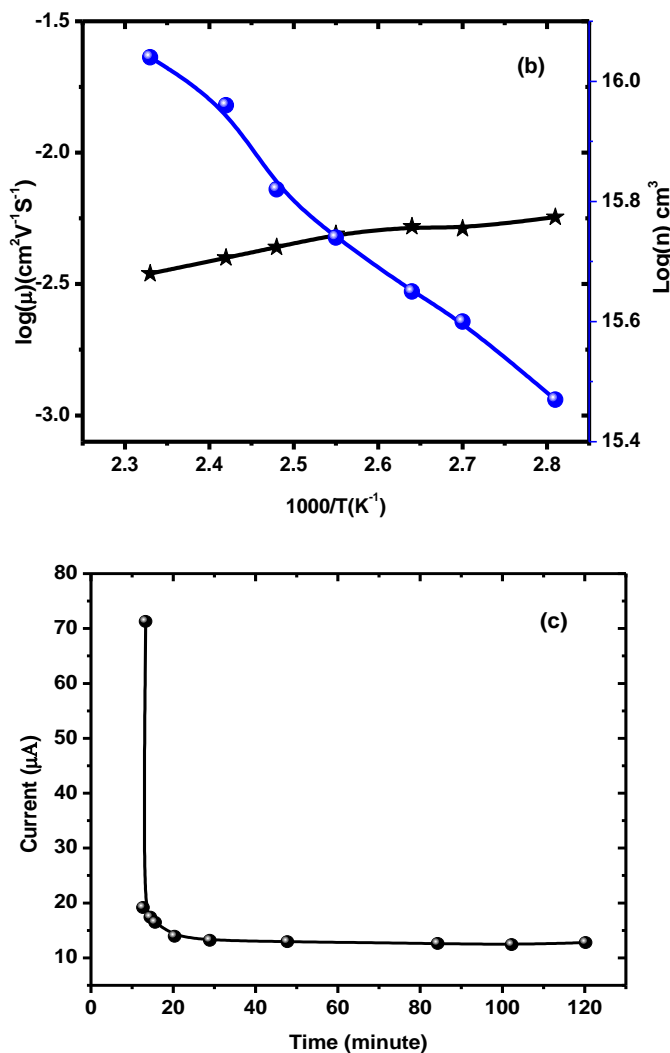


Figure 3: (a) Experimental arrangement of TIC technique, (b) Variation of mobility $\text{Log}(\mu) - 1/T$ (c) TIC plot for NPE(OCC)

The cell resistance of the film sample was measured before and after polarization using IS technique. From the two semi-circles the cell resistances $R_b \equiv R_0$ and $R_s \equiv R_b + R_i$, before and after polarization respectively, have been obtained. The cationic (Ag^+) transport number (t_+) has been evaluated with the help of equation:

$$t_+ = \frac{I_s(\Delta V - R_0 I_0)}{I_0(\Delta V - R_s I_s)}$$

Substituting the data in the equation we obtained $t_+ \sim 0.32$ for the present NPE (OCC) film: all other ionic parameters calculated experimentally are listed in Table 1.

Table 1. Room temperature values of some basic ionic parameters viz. σ , μ , n , and t_{ion} .

Film	σ (Scm^{-1})	E_a (eV)	μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	n (cm^{-3})	t_{ion}
Pure PEO	3.2×10^{-9}	NA	NA	NA	NA
SPE	2.35×10^{-5}	0.69	NA	NA	0.95
NPE	2.35×10^{-4}	0.22	2.93×10^{-3}	2.1×10^{15}	0.98

The SEM image of the pure PEO, SPE(OCC) and NPE(OCC) is shown in figure 4(a-c). It is analysed that pure PEO has a rough surface morphology with a lot of rumples and presence of crystalline and semi crystalline phases. It associated with high surface free energy and it facilitates the attachment of particle to the nucleus; in this way contribute to faster kinetics of nucleation, with the addition of salt, a dramatic improvement of surface morphology from rough to smooth is achieved. The smooth surface morphology is closely related to the reduction of PEO crystalline via the interaction between PEO segments and silver cations. Here by the addition of filler (TiO_2) crystalline phase of polymer composite further decreases i.e. amorphousity increases, it may help in ion transport in electrolyte in order to increases ionic conductivity. The EDS fingerprint along with SEM Figure 4(d) confirm the presence of composition in electrolyte. main conclusions of the study may be presented in a short Conclusion Section. In this section, the author(s) should also briefly discuss the limitations of the research and Future Scope for improvement.

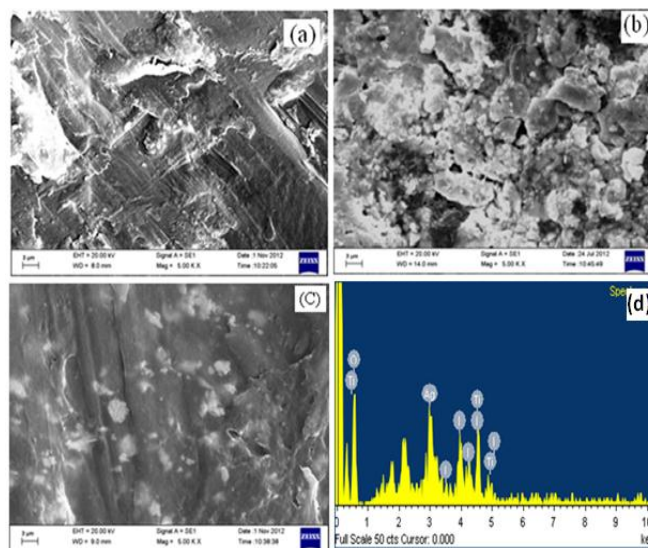


Figure 4: SEM image of (a) Pure PEO, (b) SPE(OCC), (c) NPE(OCC), (d) EDS spectra of NPE(OCC)

The best performing composition i.e. (PEO₇₀:AgNO₃₃₀)₉₇(TiO₂)₃ chosen as electrolyte for fabricating a solid state capacitor using solid polymer electrode (70PEO:30AgNO₃)₇₀(AC)₃₀ referred as PAC and egg shell membrane was used as the separator. The role of the separator is to provide minimal resistance for electrolyte ion's movement and to avoid any electrical contacts between the polymer electrolytes. The cross section view of experimental capacitor is shown in Figure 5.

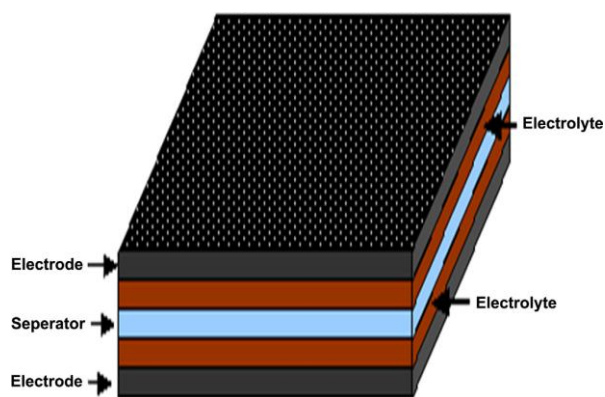


Figure 5: Schematic diagram of Solid State Capacitor with the configuration.

Electrodes of the capacitor allow a small amount of current to leak which will cause the potential decay of a charge state of the capacitor over time. Along with leakage current, another important factor is self-discharge to evaluate its performance. Ideal capacitors maintain constant potential without any flow of current from an external circuit. While real capacitors, require a current, called leakage current to maintain constant potential. We measured the leakage current and self discharge of the device by charging at 2.0 V and by monitoring the current required to maintain that specific potential. In our symmetric device, as shown in Figure 6, the leakage current dropped significantly when the potential is applied initially (from 50 μ A to 20 μ A after 200 min) and then gradually the loss in current was smaller and kept stabilizing (finally to only 5 μ A after 25 h). This value is less compared with those for reported in the literature [26–29] and it's a characteristic of electrochemical double layer formation. The self-discharge potential of the device decreases from its initial value of 2 V to 1 V relatively in a rapid manner and then slows down with time. The practical advantage of low self-discharge course is very attractive for its use in standby power etc. On the basis of physical and electrochemical studies, it can be confirmed that the newly synthesized polymer based electrodes PAC through hot press technique performed relatively well and the presence of activated carbon enhanced the ionic conductivity and Ag ion diffusion mimicking as capacitor behaviour.

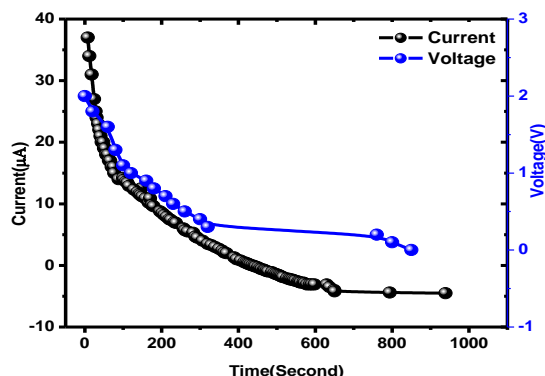


Figure 6: Leakage current profile and self discharge profile of Capacitor

Cyclic voltammetry profile of the solid-state capacitor is shown in Figure 7(a). The scan was swept at a constant rate of 0.01V/s between the voltage range 0 and 1.0 V, and the corresponding current was recorded. The electrode was started with an anodic scan at 0.2 V and finished at 1.0 V then reversed back to the original potential via cathodic scan. It is observed that shape of CV curves is nearly rectangle and symmetry or mirror image about their zero current line, which is a clear proof of well developed capacitance properties. Using relation $C = \frac{Q}{V_r \cdot m}$ specific capacitance of capacitors calculated which shows capacitance value of 5 F/g cycling.

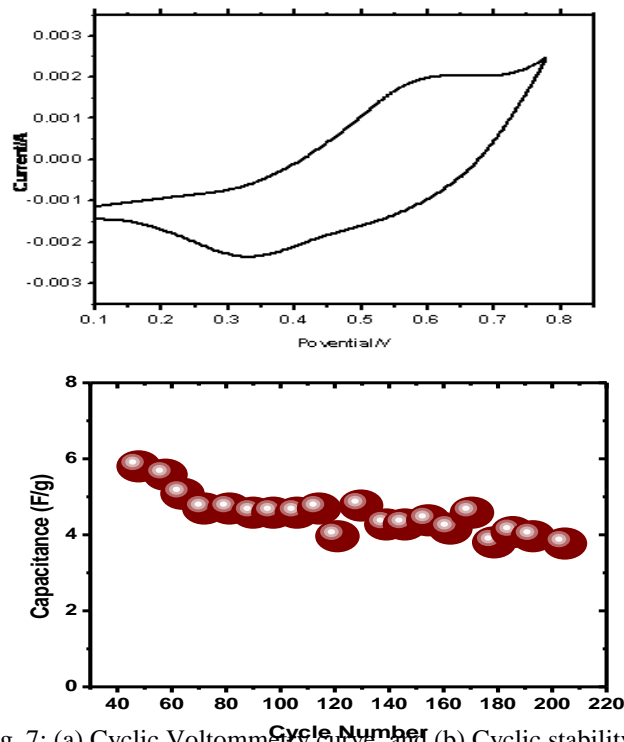


Fig. 7: (a) Cyclic Voltammetry curve and (b) Cyclic stability of experimental capacitor

The available capacitance is found to be stable over numerous cycles, and interestingly, the Coulombic efficiency is close to 92%, suggesting the all solid-state device is suitable for long-term electrochemical cycling.

IV. CONCLUSIONS

PEO- and AgNO₃-based nanocomposite polymer electrolytes with TiO₂ in different weight percentage have been synthesized by a hot press technique, and results have been reported. The optimum conducting ($\sigma \sim 2.35 \times 10^{-5}$ S/cm) composition was found for 3%TiO₂ in SPE, confirm by lowest value of activation energy. Ionic nature is confirmed by ion transference (t_{ion}) calculation. The mobility (μ) and carrier ion concentration (n) also calculated. All the physical characterization was studied on the best chosen material NPE(OCC). SEM analysis shows that the addition of inorganic filler reduces the degree of crystalline while enhancing the ionic conductivity. The best chosen electrolyte was tested in the symmetric capacitor with PAC electrode. The solid-state capacitor exhibited 5 F/g at a current density of 0.5 A/g, and the available capacitance is stable for multiple cycles. shows comparatively good performance.

REFERENCE

- [1] D. E. Fenton, J. M. Parker, P. V. Wriath, *Polymer* 14 (1973) 589.
- [2] M. P. Armand, J. M. Chabagno, M. Diadat, „Fast Ion Transport in Solids“ (Eds.) Vashistha P., Mundy J. M. and Shen G. K. (North Holland 1979) p. 135.
- [3] M. B. Armand, *Ann. Rev. Mater. Sci.* 16 (1986) 245.
- [4] M. A. Ratner, D. F. Shriver, *Int. J. Electrochem. Sci.*, Vol. 6, 2011 881
- [5] J. R. Mac Callum, C. A. Vincent, (Eds.) *Polymer Electrolyte Reviews*, Vol. 1, 2 (Elsevier Applied Science Publisher, London 1987 & 1989).
- [6] K. Murata, *Electrochimica Acta*, 40 (1995) 2177.
- [7] P. G. Bruce, *Solid State Chemistry*, (Cambridge University Press, Cambridge 1995).
- [8] F. M. Gray, *Polymer Electrolytes* (Royal Society of Chemistry Monographs, Cambridge 1997).
- [9] F. Capuano, F. Croce, B. Scrosati, *J. Electrochem. Soc.* 138 (1991) 1918.
- [10] F. Croce, G. B. Appetecchi, L. Persi, B. Scrosati, *Nature* 394 (1998) 456.
- [11] G. B. Appetecchi, F. Croce, et al., *Electrochem. Acta* 45 (2000) 1481.
- [12] G. B. Appetecchi, J. Hassoun, B. Scrosati et al., *J. Power Sources* 124 (2003) 246.
- [13] R. C. Agrawal, Angesh Chandra, *J. Physics D: Appl. Phys.* 40 (2007) 7024.
- [14] G. P. Pandey, S. A. Hashmi, R. C. Agrawal, *Solid State Ionics* 179 (2008) 543.
- [15] R. C. Agrawal, A. Bhatt, Y. K. Mahipal, *New J. Phys.* 10 (2008) 043023.
- [16] G. P. Pandey, S. A. Hashmi, et al., *J. Phys. D: Appl. Phys.* 41 (2008) 055409.
- [17] A. Chandra, R. C. Agrawal, et al., *J. Phys. D: Appl. Phys.* 42 (2009) 135107.

- [18] G. P. Pandey, R. C. Agrawal, et al., *J. Phys. D: Appl. Phys.* 43 (2010) 25550;
- [19] R. C. Agrawal, Y. K. Mahipal, Rehana Ashrafi, *Solid State Ionics* (2010) (in press).
- [20] R. C. Agrawal, G. P. Pandey, *J. Phys. D: Appl. Phys.* 41 (2008) 223001.
- [21] M. L. Verma, and N. K. Singh, *CSVTV Reaserch Journal.* (2012). 5: 22-26.
- [22] M. L. Verma M Minakshi, and N K Singh, *Electrochimica Acta* 137 (2014) 497–503.
- [23] M. L. Verma M Minakshi, and N K Singh ‘American Chemical Society’ 2014.
- [24] J. B. Wager, C. Wagner, *J. Chem. Phys.* 26 (1957) 1597.
- [25] J. Evans, C. A. Vincent, P. G. Bruce, *Polymer* 28 (1987) 2324.
- [26] A. Lewandowski, P. Jakobczyk, M. Galinski, M. Biegun, Self-discharge of elec-trochemical double layer capacitors, *Phys. Chem. Chem. Phys.* 15 (2013) 8692.
- [27] J. Kang, J. Wen, S.H. Jayaram, A. Yu, X. Wang, Development of an equivalentcircuit model for electrochemical double layer capacitors (EDLCs) with distinctelectrolytes, *Electrochim. Acta* 115 (2014) 587.
- [28] C. Meng, C. Liu, L. Chen, C. Hu, S. Fan, Highly flexible all solid state paper likepolymer supercapacitors, *Nano Lett.* 10 (2010) 4025.
- [29] J. Black, H.A. Andreas, Effects of charge redistribution on self-discharge of elec-trochemical capacitors, *Electrochim. Acta* 54 (2009) 3568.

Authors Profile

Dr. Nirbhay Kumar Singh, Presently working as Assistant Professor in Krishna Engineering College Bhilai, C.G., India. Dr. Singh has published many research papers in the field of material science and presented their thought in many national and international Conferences. Now he is actively working for the improvement of performance of energy storage devices i.e. supercapacitor, battery and ultrabattery.



Mr. Manish Kurrey, presently Assistant Professor in Kalinga University Raipur. His work in the field of power engineering are highly appreciable. He has guided many M. Tech. students at the level of research in the field of power engineering. Mr. Satpreet Singh Gill are one of the students working under him.



Mr Satpreet Singh Gill pursuing M.Tech. in power electronics from Kalinga University under the guidance of Proff. Manish Kurrey. His work in the field of power electronics are highly appreciable and he has presented many research paper in various conferences. After M. Tech. he is planning to continue his Ph.D. in the same field to satisfy his scientific desire.

