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Novel Dispersion of CeO_2 Nanofiller in PEO/PMMA Blended Nanocomposite Solid Polymer Electrolytes †

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Abstract: The present study focuses on the electrochemical performance of polyethylene oxide (PEO) - polymethyl methacrylate (PMMA) blended plasticized nanocomposite solid polymer electrolytes [BPNSPE] amid cadmium bromide ($CdBr_2$) as dopant salt along with cerium oxide (CeO_2) nanofiller. Awfully thin nanofilms of BPNSPE was signalized through distinct way of working in characterization studies such as X-ray diffractogram (XRD), Fourier transforms infrared spectroscopy (FT-IR), Ultra violet visible spectroscopy and Scanning electron micrographs (SEM). The X-ray diffractogram (XRD) confirms the formation of polymer electrolyte [PE] as well as the decrease in degree of crystalline character in BPNSPE sample and the particle dimension was calculated via Debye-Scherer equation. The structural changes and formation of complexes were inspected by Fourier transforms infrared spectroscopy (FT-IR) and ocular absorbance scrutiny was accomplished by Ultra Violet visible spectroscopy whereas the morphological structure was interpreted by scanning electron micro graphical image. The existing work is intended to be aware of the significance of CeO_2 nanofillers with the BPNSPE arrangement which is suitable for batteries and ionic devices.

Keywords: X-ray diffraction; Cerium oxide; UV; SEM

1. Introduction

Nanotechnology concept is hooked with various branches of science whereas the acquired nanotechnology might encourage various sources of synthesized nanoparticles to procure enormous utilizations in electronics, agriculture and chemical industries etc. The enduring development and comprehensive use of automobile gadgets are most significant in the field of nanotechnology to increase the requirement for secondary batteries where the electrical energy is stored [1]. Recent times Polyethylene oxide polymer is progressed significantly which is ecologically safe [2-4]. The field has expanded from the classical period and in the modern period scientists concentrated in the development of polymer electrolytes [5-6]. There are three types of polymer electrolytes [PE] namely hydro gel polymer electrolyte, liquid crystal polymers and blended composite polymers. Hydro gel polymer electrolyte and Liquid crystal polymers has high ionic conductivity but it does not have the ability of mitigating current issues when the positive electrode and negative electrode of electrolyte sample is interfaced [7]. So as to turn lucid this problem blended composite polymer electrolyte was taken into description. Blended composite PE is a form of polymer which includes salts and inorganic filers that are inert but the non-conductive constant is high in order to balance the potential by constraining the configuration of ion pairs in the form of polymeric matrices [8].

Polyethylene oxide established in the theory of electrolytes polymer which can break down assorted salts by appearing in the interactivity of EO whatever contemplated that might be the most excellent electrolyte polymers which is globally employed in battery studies. Commonly, polyethylene oxide is a semi-crystalline polymer that exhibits superior ionic conductivity and tremendous interfacial stability [9] but the stability of PEO decreases at higher temperatures. Hence, the procedure to develop the thermal establishment and crystallinity of PEO, it is blended with PMMA which is an acrylic, amorphous polymer. In particular, polymethyl methacrylate (PMMA) with its excessive tensile firmness might be acceptable to upgrade the mechanical solidity of the host polymer and it is most compatible with PEO in the melting state. In order to enhance the conductivity new inorganic salt namely $CdBr_2$ has been attempted in which Cd^{2+} ions interact with ether oxygen (EO) of PEO in order to increase the mobility of charge carriers. Several researchers attempted different ceramic nanofillers such as SiO_2, Al_2O_3, ZnO and SnO_2 [10-12] with the intention of increasing the potential and standardized stability of the blended PE. Here we utilized cerium oxide (CeO_2) which is one of the most favorable metal oxide nanofiller. It behaves as a UV-absorber and globally applied in many fields such as solar cells, catalysts, UV blockers, photo degradation of organic pollution, electronic devices [13].

This assignment targets on acknowledging the morphological and spectral investigation of BPNSPE by means of cadmium bromide ($CdBr_2$) compound and its additional assimilation of CeO_2 nanofiller by increasing the ionic conductivity and firmness by the evaluation of X-ray diffractogram, Fourier transforms infrared spectrum, Ultra violet visible spectrum along with Scanning electron micro graphical (SEM) investigations.

2. Exploration Characteristics

2.1. Chemicals Acquired

Chemicals like polyethylene oxide (PEO) whose molecular weight is 5×10^5, Polymethyl methacrylate (PMMA) whose M_n value is 996,000, cadmium bromide ($CdBr_2$) and cerium oxide (CeO_2) were brought from Sigma Aldrich for the synthesis.

2.2. Manufacture of BPNSPE Nanofilm Arrangement

Nanofilms of BPNSPE were groomed by fusing 0.2g of polyethylene oxide (PEO) and 0.1g of polymethyl methacrylate (PMMA) with 0.024g of cadmium bromide ($CdBr_2$) by the dissemination of 5 wt. % cerium oxide (CeO_2) whose size of the compound is less than 100nm. PMMA polymer was put together the stuffiness freely by placing them in vacuum drying oven at 373 Kelvin over a period of 15 minutes. Behind time, polyethylene oxide (PEO) and polymethyl methacrylate (PMMA) was liquefied in usual solvent acetone (30 ml), succeeded using unmediated mixing them for over an hour for producing a homogeneous fluid. Cadmium bromide ($CdBr_2$) sample was dried out using a vacuum drying oven at 373 Kelvin. Thereafter, the output is dissipated towards polymer blends and swirled for an hour. In that moment, 5 wt. % of cerium oxide (CeO_2) inorganic ceramic filler is added to the solid complex and it is mixed for another 2 hours and it is poured in a washed petri-dish and parched under liberated air over one day at the room temperature. In the course of time, impulsively secured samples of PEO-PMMA- $CdBr_2$-5 wt. % of CeO_2 were accomplished and safe-guarded in desiccators for further scrutinization studies. The schematic depiction of BPNSPE nanofilm is exposed in Figure 1.

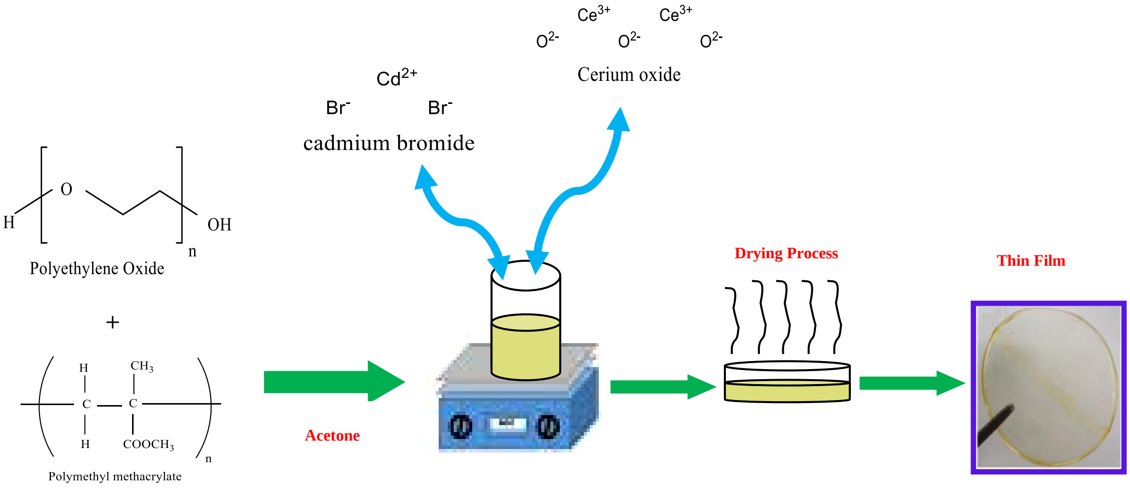

Figure 1. Schematic illustration for the preparation of BPNSPE nanofilm.

2.3. Idiosyncrasy Studies

The BPNSPE nanofilms was qualified in the recognition period which is consummated in the form of emission through Bruker X-ray diffraction appliance model in a progressive way with copper $k\alpha$ that granted, whose wavelength 1.54 Angstrom where its function is appearing in 30 milli-ampere at 2theta between the angle of 10º and 80º . Vibrational band entailed in the prototype were ascertained through collecting the data over a wide region in the method of FTIR which is progressed by using the spectrophotometer model of Bruker Tensor 27. Likewise, the structural explication of the composite is induced by the spectrophotometer apparatus of Perkin Elmer Ultra Violet spectrophotometer. The morphological dramatics of BPNSPE composites were analyzed through Hitachi-S 3400N which an illustrative of microscopy electron as well as the compound's fragmentariness portrayal were accomplished by keeping the specimen in liquid N_2 and burnished with gold particles over 30 seconds and manipulated with the electrical potential of fifteen Kilo Volts.

3. Results and Discussion

3.1. Microstructure Scrutiny of Blended Plasticized Nanocomposite Solid Polymer Electrolytes [BPNSPE]

X-ray diffraction outline procured for PEO-PMMA-$CdBr_2$ as well as PEO-PMMA-$CdBr_2$-5 wt. % CeO_2 blended plasticized nanocomposite solid polymer electrolytes [BPNSPE] is shown in Figure 2. Highly intense and sharp Bragg reflection angles scrutinized at 19.14° and 23.3° signifies the semi crystalline temperament of pure Polyethylene oxide ascribed to (120) and (112) hkl planes [14] whereas the less intense reflection peak at 13.6° [15] resembles to PMMA polymer expressing its amorphous nature. The diffraction peak viewed at 26.1° harmonized to (101) hkl plane of cadmium bromide ($CdBr_2$) salt (JCPDS File No. 10-0438). The intensity and elevation of prominent peak gets diminished in PEO-PMMA-$CdBr_2$- 5 wt. % CeO_2 blended plasticized nanocomposite solid polymer electrolytes [BPNSPE] thus stipulating that the assimilation of CeO_2 nanoparticles agitates the crystalline zone thereby increasing the disorderliness of the blended polymer electrolytes. Besides, new reflection peaks have been monitored at $2\theta = 28.65°$, 33.17°, 47.53° and 56.56° which is matched to (111), (200), (220) and (311) hkl miller indices ascribing face centered cubic unit cell of CeO_2 nanofiller as substantiated from the JCPDS File No. 81-0792. Thus, the depletion of intensity, emergence of new peaks and disorderliness of the blended polymer electrolytes may lead to enhance more conducting pathways thus making the polymer in a shapeless manner thereby flourishing the finer transit of ions as renowned from Fourier transform infrared spectroscopic examinations too.

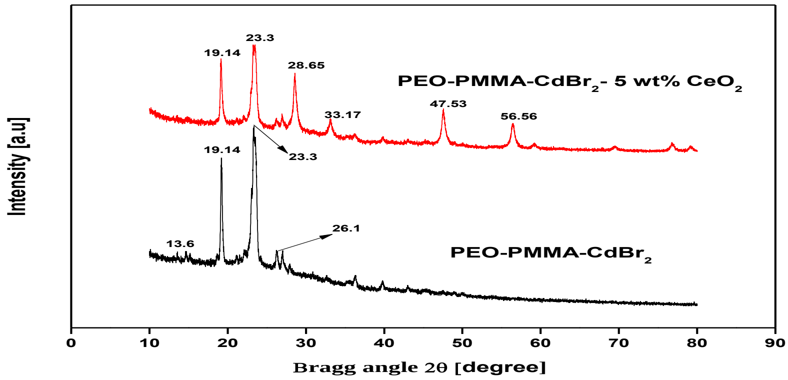

Figure 2. XRD profiles of PEO-PMMA-$CdBr_2$ and PEO-PMMA-$CdBr_2$-5 wt. % CeO_2 blended plasticized nanocomposite solid polymer electrolytes.

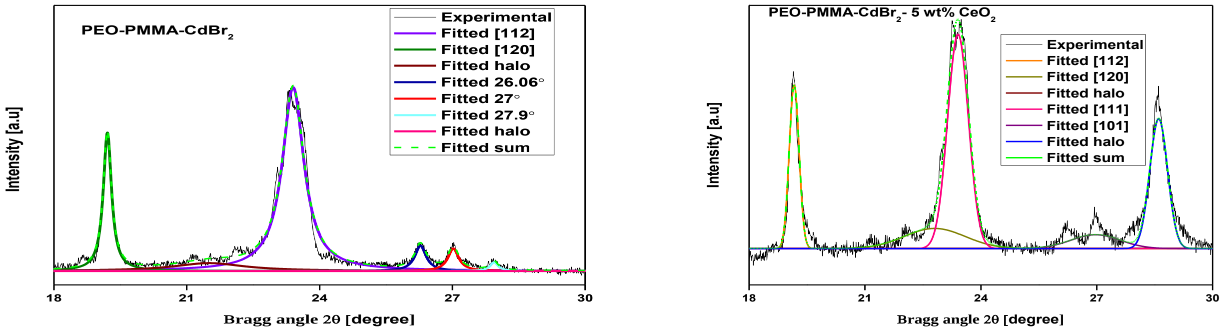

Figure 3. Deconvoluted XRD profiles acquired for PEO-PMMA-$CdBr_2$ and PEO-PMMA-$CdBr_2$-5 wt. % CeO_2 blended plasticized nanocomposite solid polymer electrolyte system.

$$L = \frac{k\lambda}{\beta \cos\theta} \rightarrow (1)$$

Here k ~ Scherrer shape factor constant ~ 0.89, λ – Wavelength of light in XRD, β-Full width at half maxima, θ – Bragg reflection angle

The size of the particle for PEO-PMMA-$CdBr_2$ and PEO-PMMA-$CdBr_2$- 5 wt. % CeO_2 BPNSPE sample has been reckoned by Debye-Scherrer formula utilizing equation 1 [16] for the most fierce peak at 19.14º by deconvolution fitting of peaks using Origin Pro 8 Software as delineated in Figure 3. The particle size of the samples are approximately 60 nm and 32 nm for PEO-PMMA-$CdBr_2$ and PEO-PMMA-$CdBr_2$-5 wt. % CeO_2 blended nanocomposite solid polymer electrolyte complex which point outs that dwindle in particle size amplifies the amorphous nature as exemplified in SEM studies as well.

3.2. *Fourier Transform Infrared Spectroscopic Results*

Fourier transform infrared spectrum in favor of PEO-PMMA-$CdBr_2$ along with PEO-PMMA-$CdBr_2$-5 wt. % CeO_2 blended nanocomposite solid polymer electrolytes [BPNSPE] is shown in Figure 4. It is discerned that significant changes has been ascertained after the assimilation of CeO_2 nanofiller into the solid polymer electrolytes. The wave number noticed at 841 cm^{-1} as well as 961 cm^{-1} correlated to C-H_2 trembling [17] and C-H_2 rotating mode appropriate to polyethylene oxide [18] and its position changes to 843 cm^{-1} and 954 cm^{-1} subsequent to the merging of CeO_2 nanofiller into the polymer matrix.

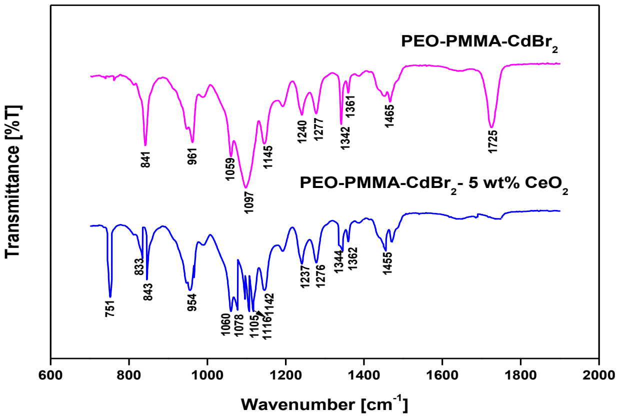

Figure 4. FT-IR transmittance spectrum of PEO-PMMA-$CdBr_2$ and PEO-PMMA-$CdBr_2$-5 wt. % CeO_2 blended plasticized nanocomposite solid polymer electrolytes.

Polyethylene oxide shows the semi conscious triad vibrational spectrum at 1145 cm^{-1}, 1059 cm^{-1} along with 1097 cm^{-1} comparable to C–O-C stretching mode of vibration [19] which gets relocated to 1142 cm^{-1}, 1060 cm^{-1} and 1105 cm^{-1} in the matrix. Similarly, the absorption peak sited at 1240 cm^{-1} and 1465 cm^{-1} ascribed to C-H_2 symmetric stretching [20] and C-H_2 scissoring mode of PEO [18] gets dislodged to 1237 cm^{-1} and 1455 cm^{-1} in the ceramic filler involved complex. Furthermore, twin bands monitored at 1342 cm^{-1} and 1361 cm^{-1} embodies C-H_2 fluttering form [21, 22] transferred to 1344 cm^{-1} and 1362 cm^{-1}. Besides, the spectrum noticed at 1277 cm^{-1} attributed near C-C-O stretching mode of vibration of PMMA [23] gets shifted to 1276 cm^{-1} whereas the peak at 1725 cm^{-1} analogous to C=O stretching of PMMA [23] disappear in the composite. Furthermore, four new spectrums viewed at 833 cm^{-1}, 751 cm^{-1}, 1078 cm^{-1} and 1116 cm^{-1} after the enclosure concerning to CeO_2 nanofiller while lower wave number vibrational peak examined at 751 cm^{-1} trait to Ce-O stretching bond [24] in the complex. The above sequels of spectral transformations may be due to the chemical reaction and structural changes taking place between EO group of PEO, - CH_3 group of PMMA polymer with Cd^{2+} cation of $CdBr_2$ and CeO_2 nanofiller as evidenced from the present XRD studies too.

3.3. Absorption Study of Blended Plasticized Nanocomposite Solid Polymer Electrolytes [BPNSPE]

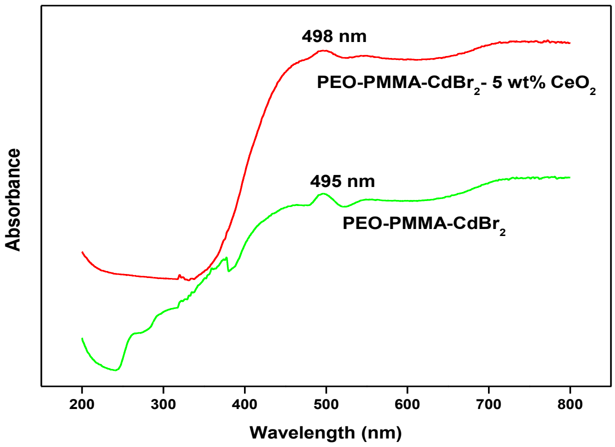

Figure 5. Optical absorption spectra of PEO-PMMA-$CdBr_2$ and PEO-PMMA-$CdBr_2$-5 wt. % CeO_2 blended plasticized nanocomposite solid polymer electrolytes.

The optical response acquired for PEO-PMMA-$CdBr_2$ and PEO-PMMA-$CdBr_2$-5 wt. % CeO_2 blended plasticized nanocomposite solid polymer electrolytes [BPNSPE] in the absorption range 200 – 800 nm is shown in Figure 5. On the whole PEO-PMMA-$CdBr_2$ sample shows absorption peak at 495 nm which increases to 498 nm after the inclusion of CeO_2 nanofiller into the polymer matrix while pure cerium oxide usually shows absorption peak around 298 nm [25] but here absorption peak has been noticed at 498 nm in PEO-PMMA-$CdBr_2$ -5 wt. % CeO_2sample because the CeO_2 filler interacts with the polymer and salt, thus shifting the peak towards longer wavelength region which is due to the lower energy level to higher energy level exhilaration of the electrons thereby increasing mobility of charge carriers. The absorption peak observed at higher wavelength range may be due to the transition of electron from 2p state valence band of O^{2-} molecule present in polymer to 4f state conduction band of Ce^{4+} of CeO_2 nanofiller [26].

3.4. Surface Morphology of Blended Plasticized Nanocomposite Solid Polymer Electrolytes [BPNSPE]

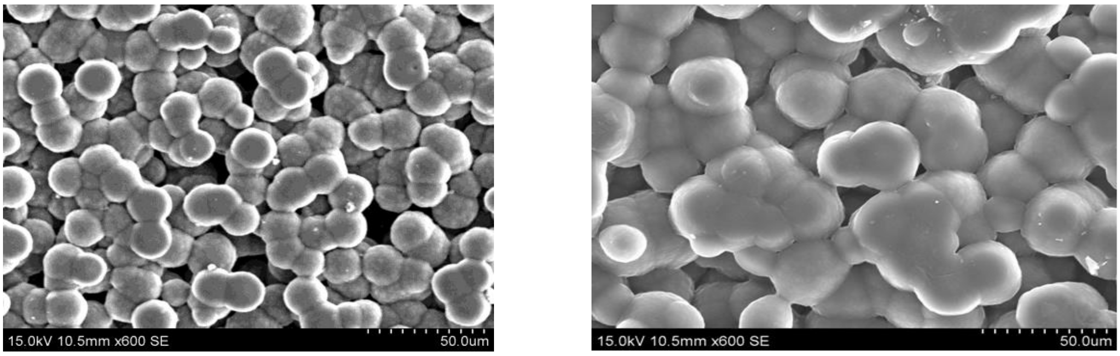

Figure 6. SEM photomicrographs appertaining to PEO-PMMA-$CdBr_2$ and PEO-PMMA-$CdBr_2$-5 wt. % CeO_2 blended nanocomposite solid polymer electrolytes.

The SEM micrographs of PEO-PMMA-$CdBr_2$ along with PEO-PMMA-$CdBr_2$-5 wt. % CeO_2 blended plasticized nanocomposite solid polymer electrolytes [BPNSPE] be exposed in Figure 6. The surface image of PEO-PMMA-$CdBr_2$ reveals the presence of compactly arranged spherical grains of approximately same size which indicates that blend is highly crystalline in nature whereas the CeO_2 integrated nanocomposite polymer electrolyte complex illustrates an astonishing improvement in terms of structural alteration from crystalline phase to unstructured phase. It is evident that owing to the accumulation concerned to CeO_2 nanofiller hooked on the complex, presence attributed to spherical grains has completely disappear which further change to a deformed shape thus indicating the reduction in crystal temperament of the blended thin film. Still, blended polymer, salt as well as nanofiller signifies the smoothened region which symbolizes the progress of ions to move in a faster rate [27] thereby ionic conductivity of BPNSPE plays a major role as evidenced amongst above results.

4. Conclusions

The electrochemical performance of blended plasticized nanocomposite solid polymer electrolyte [BPNSPE] nano emaciated films of PEO-PMMA-$CdBr_2$ and PEO-PMMA-$CdBr_2$-5 wt. % CeO_2 blended nanocomposite solid polymer electrolytes were gone through XRD, FTIR, UV and SEM investigations and the polymer matrix is found to progress with fall of crystal properties owing to CeO_2 inorganic nanofiller in the same way analyzed through above mentioned explorations. Thus, the present evaluation provides the effect of CeO_2 nanofiller on PEO-PMMA-$CdBr_2$ complex thereby the transportability of conducting electrons accelerates and hence making it as favorable compound in upcoming research.

Author Contributions*:* Conceptualization and methodology: S.A.; Validation S.A., K.R., A.Y.M.; Visualization S.A., K.R., A.Y.M.; writing—original draft preparation S.A., K.R., A.Y.M.; review and editing S.A. All authors have read and agreed to the published version of the manuscript.

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