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ORIGINAL PAPER

Effect of TiO_2 nano fillers on ionic conductivity enhancement in $Mg(BH_4)_2$:polyethylene oxide (PEO) polymer gel electrolyte

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Abstract

Temperature dependence of ionic conductivity of three different compositions of the $Mg(BH_4)_2$:polyethylene oxide (PEO):propylene carbonate (PC) polymer gel electrolyte with $Mg(BH_4)_2$:PEO molar ratios of 1:8, 1:10, and 1:12 was studied. The composition with $Mg(BH_4)_2$:PEO = 1:10 exhibited the highest ionic conductivity of 7.60×10^{-6} S cm^{-1} at 30 °C. The effect of TiO_2 nanofiller on ionic conductivity enhancement was studied for $Mg(BH_4)_2$:PEO:PC:TiO_2 polymer gel electrolyte by varying the TiO2 weight ratio from 0 to 12.5 wt.%. The highest ionic conductivity of 17.95×10^{-6} S cm^{-1} at 30 °C was exhibited by the electrolyte composition with 10 wt% of TiO_2 nanofiller. The optimized electrolytes had a Mg^{++} cationic transference number of 0.22 for the filler free electrolyte and 0.30 for the TiO_2 10wt% filler incorporated electrolyte. Both electrolytes had negligible electronic conductivity. A more than two-fold increase in the ionic conductivity and a 30% increase in Mg^{++} ion transference number can be attributed to the nanofiller effect caused by TiO_2. This preliminary study shows the possibility of developing this PEO-based polymer gel electrolyte to be used in rechargeable Mg ion batteries.

Keywords TiO_2 nanofiller · Magnesium borohydride · Poly (ethylene oxide) · Gel polymer electrolyte · Cationic transference number · Ionic conductivity

Introduction

It is predicted that among the top ten problems faced by humans in the next decade would be the energy crisis due to the depletion of conventional energy sources like fossil fuels. This is especially due to the increase in global population as well as due to the rapid development in countries like China and India which require more and more energy generated from fossil fuels for their industrial development. Fossil fuel burning for energy generation also contributes to environmental pollution with many adverse effects on humans and the biosphere [1–3]. Frequent use of fossil fuels causes the rise of the current level of CO_2 in the atmosphere leading to the greenhouse effect and global warming [1]. Therefore, the supply of clean energy will be the main challenge in the years to come for maintaining a comfortable standard of living while protecting the environment. In any case, the fast-depleting conventional energy sources based on fossil fuels will also be limited in supplying the future energy needed for the world. Therefore, developing alternative and environmentally friendly renewable energy sources such as solar and wind along with hydro and geothermal, etc. along with low energy consuming technologies and efficient energy storage methods are being widely discussed in the scientific community [4]. Ideally, electrical energy must be available 24 h a day to meet the continuous energy demand by society and industry. Therefore, greatly improved, low cost and reliable electrical energy storage systems are required. There are several types of energy storage systems including thermal storage, fuel storage, and batteries supercapacitors. Among these, batteries are devices that are used to convert chemical energy directly to electrical energy and they are the leading energy storage technologies available today that are capable of releasing a flow of charge when required. Rechargeable

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battery (secondary battery) technology is the most promising because the chemical reaction employed to generate electricity is reversible [4]. Rechargeable metal-ion batteries (Li, Na, K, Mg, Zn, Al, etc.) with a long lifetime, high energy/power density, and safety are preferred and attract much attention due to their flexibility in diverse applications. These can be used as portable devices as well as stand-alone high-capacity energy storage systems. Rechargeable batteries are also in high demand for electrical and hybrid vehicles. The most recent development in this field is the lithium-ion batteries with higher charge density and increased number of charge/discharge cycles compared to other systems. However, the limited availability of Li resources has become a serious problem for large-scale manufacturing of lithium-ion batteries for future applications [5–9]. Therefore, there has been a growing interest in the development of other alternative metal-based rechargeable batteries.

As one of the possible alternatives to lithium-ion batteries, magnesium-ion batteries (MIBs) have attracted wide attention due to their excellent safety (no dendrite formation), low cost, and high volumetric energy capacity (3833 mA h cm^{-3}). Magnesium is highly abundant in nature and can be easily extracted from the earth's crust. Moreover, magnesium is less reactive than lithium and sodium towards oxygen and humid atmospheres, therefore handling the material is easy in open air. It is a non-toxic and environmentally friendly element having almost identical ionic radii compared with that of lithium. One of the most promising characteristics of magnesium is that it is divalent, such that the oxidation reaction would result in two electrons and a Mg^{++} ion. In addition, the divalent nature of magnesium results in a high specific capacity and volumetric energy density.

However, there are some drawbacks to be overcome before magnesium batteries are developed and commercialized on a large scale. Some of these drawbacks are developing suitable Mg^{++} ion conducting electrolytes with appreciable ionic conductivity, maintaining Mg anode for stable charging and discharging process, developing Mg^{++} intercalation materials to be used as cathodes with high intercalation/de-intercalation ability with stability while increasing the low voltage values. Since magnesium is heavier than lithium, the battery will naturally be heavier for a given energy capacity. However, with a higher energy density than lithium-ion batteries, the use of magnesium-ion batteries could potentially increase the range of the electrical vehicles [10, 11].

Three types of electrolytes that are widely used in electrochemical devices can be categorized as liquid, solid, and gel. Even though liquid electrolyte shows relatively higher ionic conductivity, they also have a high risk of leakage and can cause corrosion of electrode materials. On the other hand, solid electrolytes do not have problems with electrolyte leakage, but they generally possess very low ionic conductivity at ambient temperatures due to their solid nature. To overcome these problems, polymer-based, gel polymer electrolytes (GPEs) have been developed while maintaining relatively high ionic conductivity as well as good compatibility with electrode materials. In this respect, magnesium ion-conducting gel polymer electrolytes suitable for magnesium-ion rechargeable batteries have received particular attention in recent years because of their advanced performance in charging and discharging, high power density, and high volumetric capacity [10]. Most of the conventional magnesium salt-containing electrolytes such as $Mg(ClO_4)_2$, $Mg(TFSI)_2$, or $Mg(PF_6)_2$ dissolved in carbonate or ether solvents have shown poor performance due to the reduction of these electrolytes resulting in the formation of an electronically blocking surface layer which does not conduct magnesium ions and inhibits deposition [12, 13]. In Grignard reagents (RMgX, R = alkyl or aryl group, X = halide in ethereal solvents), the reversible Mg deposition and dissolution process could be enhanced but, poor oxidative stability again limits their practical application. Some additives such as ionic liquids (IL), cross-linking agents, low molecular weight organic additives, and inorganic fillers can efficiently improve electrochemical performances and the capacity of the batteries and ionic conductivity values of the electrolytes [10, 11, 13–16]. Among them, the addition of nano-size oxide fillers such as Al_2O_3 [17, 18], TiO_2 [19, 20], SiO_2 [21, 22], and ZrO_2 [23], and low molecular weight plasticizers such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), and polyethylene glycol (PG) to the conventional polyethelene oxide (PEO)-salt matrix have been regarded as among the most promising methods to improve the ionic conductivity.

There are several reports of incorporating inorganic nanofillers into PEO:MgX polymer electrolyte systems to enhance the Mg^{++} ion conductivity. TiO_2 addition to $Mg(Tf)_2$:PEO system [24], Al_2O_3 addition to PEO:$Mg(ClO_4)_2$ system [25], MgO addition to to PEO:$Mg(ClO_4)_2$ system [26], and MgO addition to $Mg(BH_4)_2$:PEO system [27] can be cited here as examples. There are several studies on Li^+ ion conducting electrolytes incorporating TiO_2 into PEO polymer matrices to enrich the ionic conductivity. Li^+ ion conductivity enhancement was observed by the addition of TiO_2 nanofillers for LiTf:PEO [28], LiTDI:PEO [29], and $LiClO_4$:PEO [30] electrolyte systems. However, to our knowledge, TiO_2 nanofiller incorporated nanocomposite PEO polymer electrolyte based on Mg^{++} ion has been reported by only one group except this study [17, 31]. In this study, we have synthesized $Mg(BH_4)_2$:PEO as a novel Mg^{++} ion conducting polymer electrolyte and demonstrated the enhanced ionic conductivity by incorporating TiO_2 nanofillers.

To our knowledge, this is the first report of the effect of TiO_2 nanofiller on the enhancement of the ionic conductivity and increase in Mg^{++} ion transference number in the nanocomposite polymer gel electrolyte system, PEO:$Mg(BH_4)_2$:TiO_2.

Experimental

Materials

PEO (Mw–4*10^5), magnesium borohydride [$Mg(BH_4)_2$] (purity > 97%), and propylene carbonate (PC) (purity > 99%) were purchased from Sigma–Aldrich and used as starting materials along with titanium dioxide (TiO_2 -P_{25}) nanofiller.

Preparation of electrolyte

Before use, PEO polymer, $Mg(BH_4)_2$ salt, and TiO_2 nanofiller were vacuum dried at 50 °C. Different amounts of $Mg(BH_4)_2$ and a constant amount of tetrahydrofuran (THF) were mixed and magnetically stirred for 12 h. Then, PEO (0.1 g), PC (0.8 g), and acetonitrile were mixed and magnetically stirred for 12 h. Different weights of $Mg(BH_4)_2$ shown in Table 1 were added to this polymer–solvent mixture and magnetically stirred for 12 h. Samples were then vacuum dried at 50 °C for 6 h. Compositions of the four samples prepared are given in Table 1. One sample was also prepared without adding PC.

The ionic conductivity of the three polymer electrolyte samples A, B, and C were measured as a function of temperature, and the highest ionic conductivity sample was selected for further study. Out of the three samples, sample B with salt:polymer composition molar ratio ($Mg(BH_4)_2$):PEO = 1:10 showed the highest ionic conductivity in the measured temperature range from room temperature up to 60 °C. Electrolyte sample D (a "solid" polymer electrolyte) prepared with the same salt:polymer molar ratio but without PC solvent was also vacuum dried similarly and its conductivity was also measured for comparison. Nanocomposite polymer electrolytes were prepared (Table 2) by adding different amounts of TiO_2 nanofiller (0, 2.5, 7.5, 10, and 12.5 wt. %) to the $Mg(BH_4)_2$:PEO = 10:1 (molar) electrolyte with PC in the weight ratio of PEO:PC = 1:8 (by wt) mixtures and magnetically stirring for 12 h without heating until a homogenous gel electrolyte was formed. The solvent-free gel electrolyte was prepared by vacuum drying the prepared electrolyte at 50 °C for 6 h using aluminum foil covered by a glass ring.

Table 1 Electrolyte composition prior to adding TiO_2

Sample	($Mg(BH_4)_2$)/g	Molar ratio ($Mg(BH_4)_2$):PEO	PEO/g	PC/g
A	0.015	1:8	0.100	0.800
B	0.012	1:10	0.100	0.800
C	0.010	1:12	0.100	0.800
D	0.012	1:10	0.100	0.000

Table 2 Electrolyte composition after adding TiO_2 filler

Sample no	TiO_2 weight %	TiO_2/g	($Mg(BH_4)_2$)/g	PEO/g	PC/g
1	0	0.000	0.012	0.100	0.800
2	2.5	0.023	0.012	0.100	0.800
3	7.5	0.069	0.012	0.100	0.800
4	10.0	0.092	0.012	0.100	0.800
5	12.5	0.115	0.012	0.100	0.800

Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range from 0.1 Hz to 10 M Hz by using a computer-controlled Metrohm Autolab (PGSTAT 128N). For impedance measurements, the gel electrolyte was poured onto a plastic ring of known diameter and sandwiched between two polished stainless steel (SS) blocking electrodes with the configuration SS/Gel polymer electrolyte (GPE)/SS. Then it was placed in a furnace and the temperature was changed by 5 °C intervals starting from 30 °C and ending to 65 °C. Impedance measurements were taken at each 5 °C intervals. Resistance values at each temperature were extracted from the high-frequency intercepts of the Nyquist plots, and the conductivity values were calculated.

Electronic contribution to the total conductivity of the gel electrolyte was determined by the DC polarization analysis. The polymer electrolyte was sandwiched between two stainless steel (SS) blocking electrodes with the configuration SS/GPE/SS, and polarization of the cells was accomplished by applying a 0.5 V DC across the cell over 1 h. DC polarization current was monitored as a function of time and the total ionic transference number (t_{ion}) of the polymer electrolyte was estimated by Wagner's method using the equation,

$$t_{\text{ion}=}\frac{I_i - I_f}{I_i} \tag{1}$$

where I_i is the initial current and I_f is the final steady state current. The Mg^{++} ion transference number of the gel polymer electrolyte was determined by the combination of AC and DC measurements. The cation transference number was calculated using the following equation.

$$t_{Mg^{++}=}\frac{I_s(\Delta V - r_0 I_0)}{I_{0(\Delta V - r_s I_s)}} \tag{2}$$

where I_0 and I_s are the initial and final steady state currents, and r_0 and r_s are the cell resistance before and after applying the polarization voltage, respectively. For finding the r_0 value, the electrolyte was sandwiched between two non-blocking Mg electrodes with the cell configuration Mg/GPE/Mg, and the complex impedance response of the symmetrical cell assembly was measured.

X ray diffraction (XRD) studies

XRD measurements were performed on the filler-free PEO:$Mg(BH_4)_2$ sample and PEO:$Mg(BH_4)_2 + TiO_2$ 10%wt filler added sample in order to check the effect of crystallinity due to the addition of the nanofiller.

Results and discussion

Characterization of gel polymer electrolyte

Ionic conductivity

Figure 1(a) shows the variation of ln(σ) with 1/*T* for the three gel polymer electrolyte(GPE) samples with molar ratios ($Mg(BH_4)_2$):PEO = 1:8, 1:10 and 1:12. Out of the three samples, the sample with ($Mg(BH_4)_2$):PEO = 1:10 molar ratio exhibits the highest ionic conductivity in the measured temperature range from 30 to 65 °C. The ionic conductivity of electrolyte sample D, prepared without adding PC, shows the lowest ionic conductivity of 1.485×10^{-6} S/cm at 30 °C evidently due to the solid nature of the electrolyte.

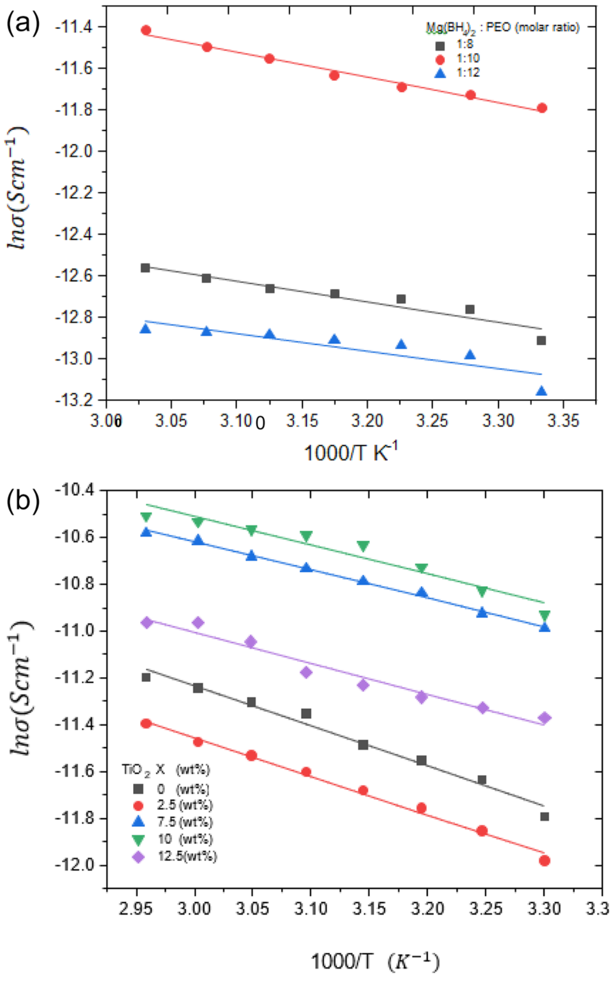

Fig. 1 Variation of ln *σ* vs 1/*T* for the prepared gel polymer electrolyte(GPE) samples **a** with molar ratios ($Mg(BH_4)_2$):PEO = 1:8, 1:10 and 1:12 incorporating PC in the weight ratio PEO:PC = 1:8. **b** With molar ratio ($Mg(BH_4)_2$):PEO = 1:10, with PC for different amounts of the TiO_2 filler wt%: 0, 2.5, 7.5, 10.0, and 12.5

The linear relationship between ln*σ* and 1000/*T* of the graph in Fig. 1(a) confirm that the temperature dependence of the conductivity obeys the classical Arrhenius relation expressed by the equation

$$\sigma = \sigma_o \exp\left(-E_a/RT\right) \tag{3}$$

where σ_o is the dc conductivity of the pre-exponential factor, E_a is the activation energy, *T* is the absolute temperature, and *R* is the Boltzmann constant.

From Fig. 1(a), it can be seen that, out of the three gel polymer electrolyte samples studied, the sample with molar ratio $Mg(BH_4)_2$:PEO = [1:10] with PC shows the highest ionic conductivity at all measured temperatures with a value of 7.564×10^{-6} S cm^{-1} at 30 °C. The GPE sample with molar ratio $Mg(BH_4)_2$:PEO = 1:12 (with PC) has a lower salt concentration and therefore a lower number of mobile ionic species/volume of the sample which contributes to the ionic conductivity. On the other hand, the GPE sample with molar ratio $Mg(BH_4)_2$:PEO = 1:8 (with PC) has a higher number of ionic species/volume which forms ion pairs and higher ionic aggregates, thereby reducing the ionic conductivity. However, at the intermediate molar ratio $Mg(BH_4)_2$:PEO = 1:10, we can expect the optimum number of mobile ionic species resulting from ionic dissociation which makes the highest contribution to the ionic conductivity (Table 3).

Figure 1(b) shows the temperature dependence of ionic conductivity of the optimized gel polymer electrolyte (molar ratio, $Mg(BH_4)_2$:PEO = 1:10 and with PC) with the addition of different amounts of TiO_2 P_{25} nanofiller at different weight ratios from 0 to 12.5%. Initially, the conductivity drops due to the addition of 2.5 wt% of TiO_2, but after this, the conductivity shows an increase up to 10 wt % TiO_2 and then starts to decrease again. A clear conductivity maximum can be seen at 10 wt % TiO_2 filler concentration with the

Table 3 The variation of ionic conductivity vs salt ratio before adding the TiO_2 filler at 30 °C

Sample	Salt ratio ($Mg(BH_4)_2$):PEO	PEO/g	PC/g	Conductivity × 10^{-6}/S cm^{-1} at 30 °C
A	1:8	0.100	0.800	2.464
B	1:10	0.100	0.800	7.564
C	1:12	0.100	0.800	1.918
D	1:10	0.100	0.000	1.485

Table 4 Ionic conductivity values at 30 °C for the TiO_2 nanofiller free and filler added gel polymer electrolyte samples $Mg(BH_4)_2$:PEO = 1:10, with PC

Sample no.	TiO_2 weight %	PEO/g	PC/g	Conductivity × 10^{-5}/S cm^{-1}
1	0	0.100	0.800	0.7564
2	2.5	0.100	0.800	0.6268
3	7.5	0.100	0.800	1.691
4	10	0.100	0.800	1.795
5	12.5	0.100	0.800	1.288

highest value of 17.95 × 10^{-4} S cm^{-1} at 30 °C. Further addition of TiO_2 has reduced the ionic conductivity value, while the electrolyte also becomes mechanically more solid-like. Figure 3 shows the corresponding conductivity isotherms of the TiO_2 nanofiller added polymer gel electrolyte along with the filler free electrolyte. Table 4 shows the ionic conductivity values at 30 °C for the filler free and filler added gel polymer electrolyte samples.

The highest conductivity among the TiO_2 nanofiller incorporated composite gel polymer electrolytes was obtained for the sample containing 10 wt % of TiO_2 (with respect to the total weight of the filler free electrolyte sample). It is well known that the addition of nano filler decreases the crystallinity of PEO and increases the amorphous phase content [25, 28]. This will favor the ionic mobility and in turn enhance the ionic conductivity. Another possible conductivity enhancement mechanism which quite likely to operate is due to the creation of transient hopping sites and additional conducting pathways through Lewis acid–base type interactions by cationic species with TiO_2 nano particles similar to the case of several PEO-based Li^+ ion systems [25, 28, 32]. Both these mechanisms are expected to contribute to the increase in the ionic mobility and cationic conductivity in the material.

From the conductivity isotherms shown in Fig. 2 it can be seen that as 2.5 wt% of TiO_2 nanofiller is introduced into the $Mg(BH_4)_2$:PEO (1:10) + PC polymer gel electrolyte, the conductivity shows a small drop. This may be due to the dilution effect in the electrolyte medium combined with the insufficient number of transient bonding sites which are needed to form continuous conducting pathways for the cationic mobility. Similar initial drop in conductivity has been reported for the PEO:tetrapropyl ammonium iodide salt:Al_2O_3 nanofiller system [33].

The variation of the activation energy with the TiO_2 nanofiller concentration is shown in Fig. 3. The lowest activation energy values correspond to the TiO_2 nanofiller concentrations of 8 wt% and 10 wt%. The initial drop in activation energy can be associated with the reduction of crystallinity of PEO and the increase in the amorphous phase content in the filler added electrolyte. This will lower the activation energy for cation migration due to the more viscous nature of the amorphous phase. After reaching the lowest activation energy value, which corresponds to the highest ionic conductivity, a further increase in TiO_2 nanofiller concentration would introduce the blocking action for cation transport and also restrict the segmental motion of the PEO polymer chains thereby increasing the activation energy and resulting in a reduction of the ionic conductivity.

The subsequent increase in conductivity due to the incorporation of TiO_2 nanofiller up to 10wt% can be due to the formation of transient bonds between H/OH surface groups of titania grains and mobile Mg^{++} cations due to Lewis acid–base type interactions which provide additional high conducting pathways as reported by several other groups for Li^+ ion containing nanocomposite polymer electrolytes [25, 32–35].

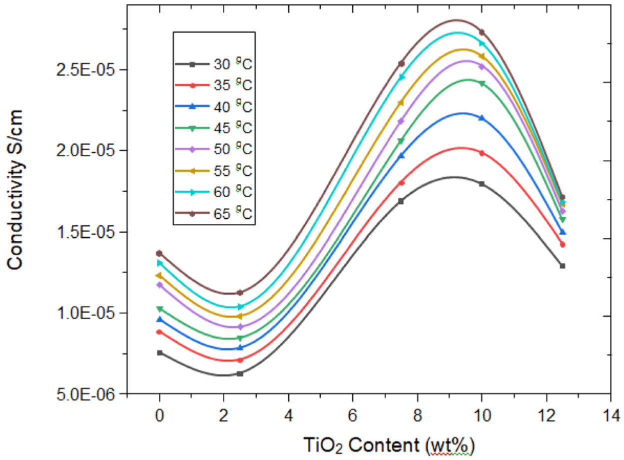

Fig. 2 Conductivity isotherms of the TiO_2 nanofiller added polymer gel electrolyte along with the filler free electrolyte. Electrolyte composition: $(Mg(BH_4)_2)$:PEO = 1:10 with PC, for different amounts of the TiO_2 filler wt%: 0, 2.5, 7.5, 10.0, and 12.5

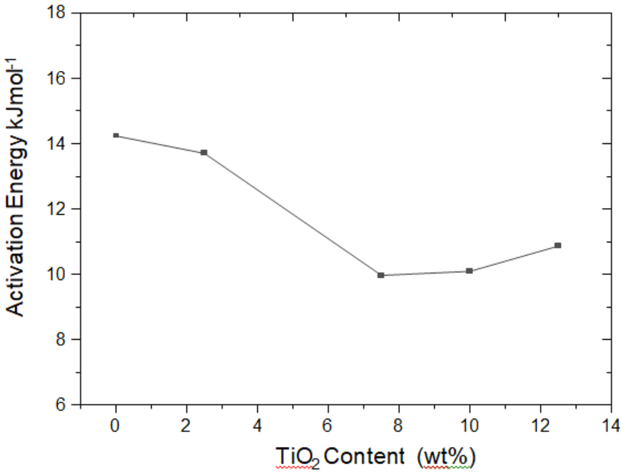

Fig. 3 Activation energy vs nanofiller concentration for the $(Mg(BH_4)_2)$:PEO = 1:10 with PC, for different amounts of the TiO_2 filler wt%: 0, 2.5, 7.5, 10.0, and 12.5

The addition of plasticizer such as ethylene carbonate (EC) or propylene carbonate (PC) to a PEO-based polymer electrolyte, in general, helps to increase the amorphous phase content of the electrolyte leading to increased segmental mobility of the polymer chains, thus favoring the ionic mobility. However, the incorporation of plasticizers would deteriorate the mechanical strength of the polymer electrolyte film while on the other hand, the incorporation of nano-size ceramic fillers has been found to improve the mechanical strength of the polymer electrolyte films [11, 25, 26, 32]. Therefore, one of the best strategies to increase the ionic conductivity in a polymer electrolyte while retaining the mechanical strength is through the addition of both a plasticizer and ceramic filler together into the polymer matrix as demonstrated by the present work. Propylene carbonate (PC) and ethylene carbonate (EC) are widely used as plasticizers in PEO-based gel polymer electrolytes to enhance the ionic conductivity [36, 37]. Out of these, PC (a liquid at room temperature) has a higher dielectric constant compared to EC (solid) and therefore has the ability to contribute for greater dissociation of the ionic salt in the electrolyte.

TiO_2 nanofiller is reported to have a high Lewis-acid character [12] compared to other commonly used ceramic fillers such as Al_2O_3, SiO_2, and ZrO_2. Therefore, incorporation of TiO_2 may lead to a higher number of transient conducting pathways for cation migration due to the Lewis acid–base type interactions between the polar surface groups of the filler and the ionic species in the electrolyte, as originally proposed by Wieczorek et al. [32].

As proposed by Wieczorek et al. and further developed by others, it is very likely that Lewis acid–base type interactions between migrating ionic species and O/OH groups at the titania grain surface are responsible for the observed conductivity enhancement [32]. An additional contribution could also come from the lowering of glass transition temperature (T_g) and the increase in the amorphous phase of the polymer electrolyte due to the presence of TiO_2 filler.

However, any increase in anionic conductivity, in this case, the $(BH_4)^-$ ion conductivity, can only be due to the increase in the PEO amorphous phase content because the $(BH_4)^-$ ions are expected to migrate in the electrolyte medium by ionic diffusion which is facilitated by the amorphous phase of the electrolyte medium. The apparent diffusion coefficient of $(BH_4)^-$ is expected to increase with the addition of TiO_2 nano filler because of the increase in the PEO amorphous phase. The reduction of the ionic conductivity at higher TiO_2 concentrations after reaching the maximum conductivity is very likely due to the blocking effect caused by the closeness of the nano TiO_2 particles and their aggregates distributed in the electrolyte medium. The corresponding variation of the activation energy is shown in Fig. 3.

XRD results

The main crystallinity peak of PEO in the XRD spectrum can be seen at 2θ = 19.18°. It is clear from the results of the XRD spectrum shown in Fig. 4 that the intensity of the main crystallinity peak of the pure PEO polymer seen around 2θ = 20° in the polymer-salt system has diminished in intensity due to the presence of the TiO_2 nanofiller, indicating the increased amorphous nature of the filler added electrolyte.

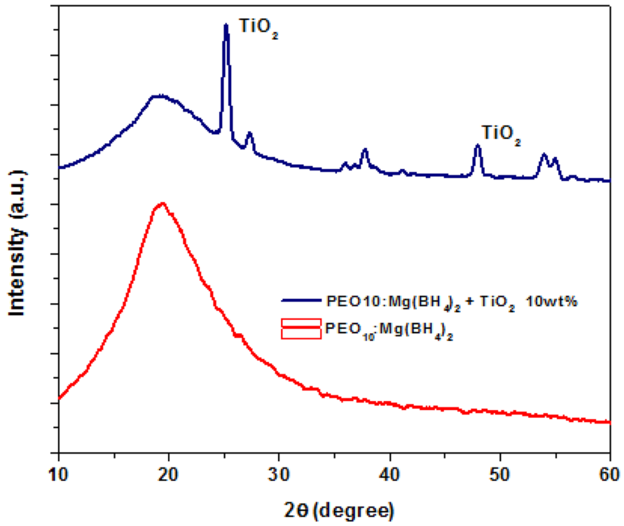

Fig. 4 XRD results of PEO_{10}:$Mg(BH_4)_2$ + PC and the filler incorporated polymer gel electrolyte PEO_{10}:$Mg(BH_4)_2$ + TiO_2 10wt% + PC showing the reduced crystallinity of the electrolyte due to the addition of the TiO_2 nanofiller

DC polarization results

Figure 5 shows the results of DC polarization measurements taken with stainless steel (SS) electrodes using the symmetrical cell configuration, SS/Electrolyte/SS under

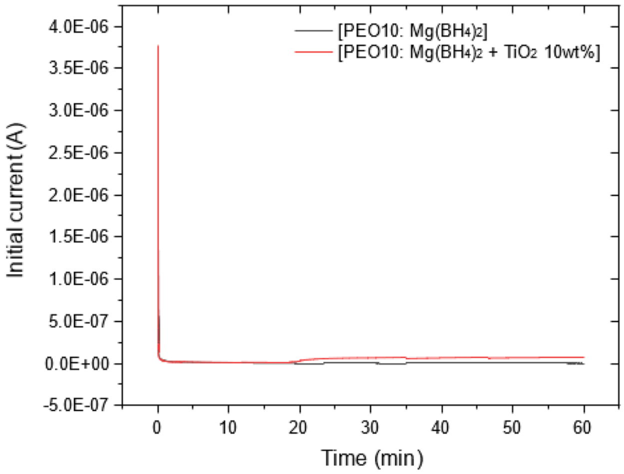

Fig. 5 DC polarization curves of the filler free gel polymer electrolyte PEO_{10}:$Mg(BH_4)_2$ + PC and the filler incorporated polymer gel electrolyte PEO_{10}:$Mg(BH_4)_2$ + TiO_2 10wt% + PC with stainless steel (SS) blocking electrodes

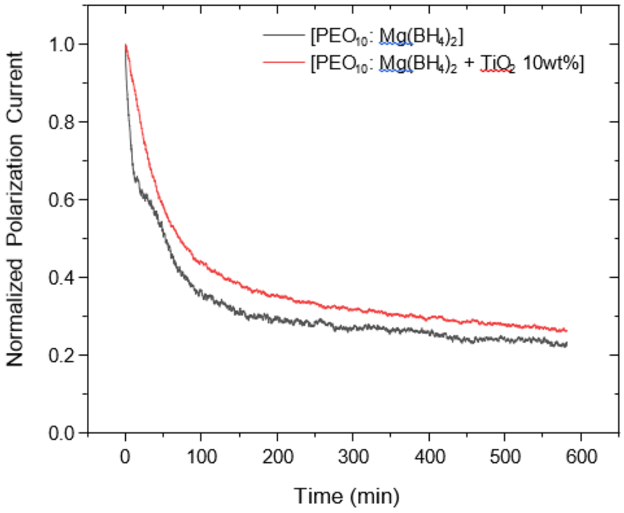

Fig. 6 Variation of the DC polarization current (normalized) as a function of time for the filler free gel polymer electrolyte PEO$_{10}$:Mg(BH$_4$)$_2$ + PC and for the filler incorporated gel polymer electrolyte PEO$_{10}$:Mg(BH$_4$)$_2$ + TiO$_2$ 10wt% + PC with Mg/Mg non-blocking electrodes

an applied voltage of 0.5 DCV. The total ionic transference number, t_{ion}, was estimated using the Eq. (1) and the values obtained are t_{ion} = 0.970 for the filler free electrolyte, [(PEO)10:Mg(BH$_4$)$_2$ + PC] and t_{ion} = 0.998 for the filler incorporated electrolyte [(PEO)10:Mg(BH$_4$)$_2$ + 10wt% TiO$_2$ + PC]. Here I_i and I_f refer to the initial current (at time 0) and final steady state current after 60 min. This shows that the electrolyte material is predominantly an ionic conductor with Mg^{2+} and BH$_4^-$ and as the dominant mobile ionic species. The total ionic conductivity of the electrolyte is made up of individual ionic conductivity contributions from these two ionic species. According to these results, the nanofiller added electrolyte with 10wt% TiO$_2$ is a better ionic conductor with a higher ionic transference number compared to the filler free electrolyte. This is very likely due to the enhanced ionic dissociation in the material due to the presence of TiO$_2$ [38].

Figure 6 shows the DC polarization curves taken for the gel polymer electrolytes with Mg/Mg electrodes in the symmetrical cell arrangement Mg/GPE/Mg with filler free and filler 10 wt% TiO$_2$ filler added electrolytes. Current vs time measurements were taken under 0.5 VDC bias voltage and the initial current I_0 (at time 0) and resulting steady state current I_f (after 3 h) were recorded.

The total ionic transference number, t_{ion}, was estimated using the equation The cation transference number t_+ can be calculated as follows: $t_+ = i_s/i_0$, where i_0 and i_s are the initial and steady-state cell currents, respectively. As seen from Table 5, the values obtained are t_+ = 0.22 for the filler free gel electrolyte, (PEO)10:Mg(BH$_4$)$_2$ + PC and t_+ = 0.30 for the filler incorporated gel electrolyte (PEO)10:Mg(BH$_4$)$_2$ + 10wt% TiO$_2$ + PC.

It is clear from Fig. 6 and Table 5 that the incorporation of the 10 wt% TiO$_2$ nanofiller has increased the cationic transference number of the electrolyte substantially from 0.22 to 0.30. According to the DC polarization measurements, the Mg^{2+} ion transference number for electrolyte [(PEO)$_{10}$ Mg(BH$_4$)$_2$] was 0.22 and for [(PEO)$_{10}$ Mg(BH$_4$)$_2$ + 10wt% TiO$_2$] was 0.30. This shows that the Mg^{2+} ion contribution to the total ionic conductivity is significant for the electrolyte incorporated with TiO$_2$. This can be attributed to the increased ionic dissociation by the nanofiller creating more cations and anions available for conduction. Another contributing factor is the creation of more transient sites for Mg^{++} ion hopping due to the formation of Lewis acid–base type interactions between the OH groups on the TiO$_2$ surface and Mg^{++} ionic species.

Dissanayake et al. have reported the conductivity enhancement in the composite polymer electrolyte PEO:Mg(ClO$_4$)$_2$ with 10 wt% of Al$_2$O$_3$ nano filler. The ionic conductivity was improved about 20 times to ~2 × 10^{-6} S cm^{-1} with addition of 10 wt% Al$_2$O$_3$. The increase in conductivity was interpreted as largely due to surface interactions between –OH functional groups on the Al$_2$O$_3$ surface and ionic species [25]. Ionic conductivity values of PEO:MgX salt:nanofiller-based polymer electrolyte systems are shown in Table 6.

In order to confirm the Mg^{2+} ion conduction in [(PEO)$_{15}$:Mg(BH$_4$)$_2$ + 10wt %TiO$_2$] electrolyte system, impedance spectroscopy was performed. Figure 7(a) shows a typical complex impedance plot of [(PEO)$_{10}$ Mg(BH$_4$)$_2$ + 10wt% TiO$_2$] at 27 °C taken with a stainless steel blocking electrode. The impedance plot consists of a low-temperature spike and a high-frequency semicircle. Figure 7(b) shows the comparative impedance plots for the symmetrical cells consisting of [(PEO)$_{10}$ Mg(BH$_4$)$_2$ + 10wt% TiO$_2$] gel polymer electrolyte with blocking (SS) and non-blocking (Mg) electrodes. The steep rising impedance pattern of SS/[(PEO)$_{10}$ Mg(BH$_4$)$_2$ + 10 wt% TiO$_2$]/SS symmetrical cell indicates the ion-blocking nature of SS electrodes to the Mg^{2+} ions at the electrode–electrolyte interfaces. The semicircular dispersion curve obtained for the

Table 5 Electronic transference number of the two polymer gel electrolytes (a) PEO$_{10}$:Mg(BH$_4$)$_2$ + PC and (b) PEO$_{10}$:Mg(BH$_4$)$_2$ + TiO$_2$ 10wt% + PC

Sample	Initial current (I_o)/A For Mg/Mg	Steady current (I_s)/A For Mg/Mg	Electronic transference number	Cationic transference number
[PC:PEO:Mg(BH$_4$)$_2$]/non filler electrolyte	1.77E-6	3.91E-7	0.0036	0.22
[PC:PEO:Mg(BH$_4$)$_2$]/TiO$_2$–10 wt % filler electrolyte	2.19E-6	5.76E-7	0.0017	0.30

Table 6 Ionic conductivity values of PEO:MgX salt:nanofiller-based polymer electrolyte systems

Mg salt	Polymer host	Nano filler	Ionic conductivity (S cm^{-1} at RT)	Cationic transp no: t_+	Cell electrodes	Ref
$Mg(Tf)_2$	PEO	TiO_2	2.8×10^{-6}	0.37		[24]
$Mg(ClO_4)_2$	PEO	Al_2O_3	1.5×10^{-4}			[25]
$Mg(ClO_4)_2$	PEO	MgO	2×10^{-6}			[18]
$Mg(BH_4)_2$	PEO	MgO	--	--	Mg/Mo_6S_8 cell	[19]

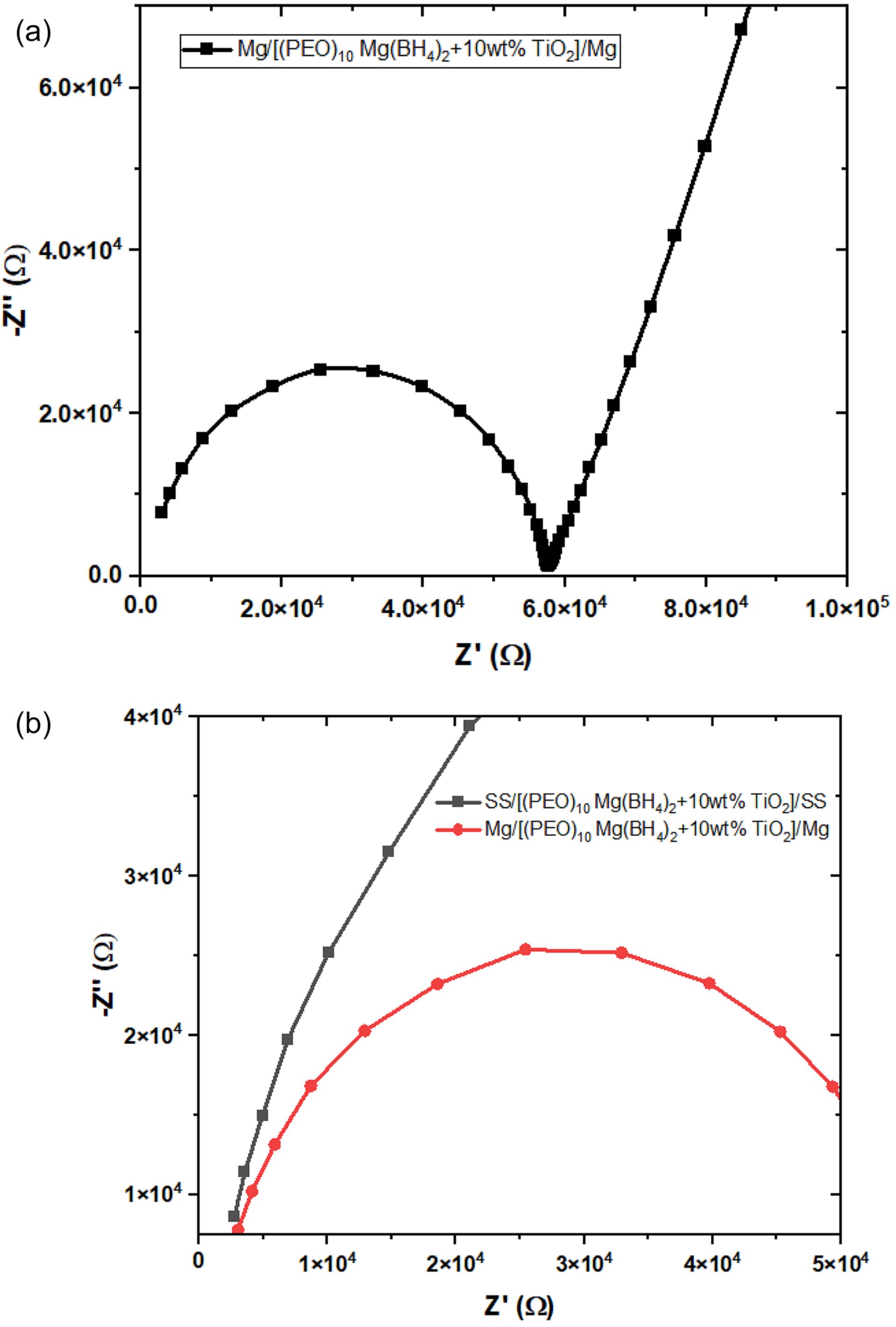

Fig. 7 **a** Typical complex impedance plot of $[(PEO)_{10}\ Mg(BH_4)_2+10wt\%\ TiO_2]$ at 27 °C taken with stainless steel blocking electrode **b** comparative impedance plots for the symmetrical cells consisting of $[(PEO)_{10}\ Mg(BH_4)_2+10wt\%\ TiO_2]$ gel polymer electrolyte with blocking (SS) and non-blocking (Mg) electrodes

Table 7 Ionic conductivity and effect of TiO_2 nano filler for ionic conductivity for different polymer matrices

Polymer used	Conducting ion	Conductivity before adding nano filler/S cm^{-1}	Nano filler	Conductivity after adding nano filler/S cm^{-1}	Reference
PEO[a]	Mg^{++}	7.6×10^{-6}	TiO_2	1.79×10^{-5}	This study
PEO	Mg^{++}	2.77×10^{-6}	TiO_2	$1.53\ 10^{-5}$	[24]
PMMA[b]	Mg^{++}	10^{-7}	TiO_2	1.78×10^{-6}	[31]
PVA[c]/chitosan	Mg^{++}	7.34×10^{-5}	No filler		[39]
Cellulose acetate	Mg^{++}	9.19×10^{-4}	No filler		[40]
Methyl cellulose	Mg^{++}	2.61×10^{-5}	No filler		[41]
PEO	Li^+	4.9×10^{-5}	TiO_2	1.6×10^{-4}	[28]
PEO	Li^+	2.05×10^{-6}	TiO_2	2.11×10^{-5}	[29]
PEO	Li^+	1.28×10^{-5}	TiO_2	8.5×10^{-5}	[30]
PMMA/PVAc[d]	Li^+	1.03×10^{-4}	TiO_2	4.45×10^{-4}	[42]
PVA	H^+	5.17×10^{-5}	TiO_2	5.52×10^{-3}	[43]
(PVDF-HFP)[e]	Zn^{++}	1.5×10^{-5}	TiO_2	3.4×10^{-4}	[44]

[a] Polyethylene oxide

[b] Polymethyl methacrylate

[c] Polyvinyl alcohol

[d] Polyvinyl acetate

[e] Poly(vinilydene fluoride- co -hexa fluoro propylene)

$Mg/[(PEO)_{10}\ Mg(BH_4)_2+10wt\%\ TiO_2]/Mg$ shows the reversible nature of the Mg electrodes in the polymer electrolyte [13].

Mg^{++} ion conductivity and comparison of different ionic conductivity values before and after incorporating TiO_2 fillers are shown in Table 7. According to the data presented in Table 7, the highest Mg^{++} ion conducting nanocomposite polymer electrolyte is reported by this research.

The enhancement of cationic conductivity due to the incorporation of TiO_2 nanofiller can also be explained as follows. In the case of the Mg^{++}-containing PEO polymer complex, Mg^{++} ion is supposed to migrate by making and breaking transient bonds with the ether oxygen of the PEO chain supported by the segmental flexibility of the PEO chain. This process is further facilitated in the TiO_2 filler added Mg^{++} ion polymer electrolyte, as the surface oxygen on the TiO_2 nanofiller surface can form additional transient bonds with Mg^{++} ions and help for Mg^{++} ion migration through the polymer matrix network. This percolation mechanism would enhance the ionic conductivity of the nanofiller added polymer electrolyte up to a certain threshold concentration of TiO_2 filler. If the TiO_2 filler concentration is increased above this limit, the "blocking action" by the presence of excessive nanofillers will hinder the ionic transport and reduce the ionic conductivity [45].

Conclusions

A novel magnesium ion conducting solid nanocomposite polymer electrolyte of composition $[(PEO)_{10}:Mg(BH_4)_2 + 10\%TiO_2]$ has been synthesized and characterized. The incorporation of titanium dioxide nanofiller into $PEO:Mg(BH_4)_2$:PC polymer electrolyte has resulted in a significant enhancement in the ionic conductivity of the parent electrolyte with the value of 7.60×10^{-6} S/cm (without filler) and 1.79×10^{-5} S/cm (with 10 wt %) at room temperature (30 °C). According to the DC polarization test, the transference number data indicate that the conduction is predominantly due to ions rather than electrons. The observed ionic conductivity enhancement due to the incorporation of the TiO2 nanofiller can be attributed to the increase of the amorphous phase content and decrease of crystallinity of the PEO-based electrolyte due to addition of TiO_2 nanofiller. In addition, the filler may also provide extra transient hopping sites due to the formation of Lewis acid-type bonds between the OH groups on the nanofiller surface and Mg^{++} ions. This is supported by FTIR data of filler free and filler added (TiO_2 10 wt %) electrolytes.

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