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Nanocomposite Polymer Electrolyte Doped with Nanosized $Li_{0.1}Ca_{0.9}TiO_3$ for Lithium Polymer Batteries

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A poly(ethylene oxide) (PEO)-based nanocomposite polymer electrolyte (NCPE) doped with nanosized $Li_{0.1}Ca_{0.9}TiO_3$, a lithium fast ionic conductor, has been developed. The ionic conductivity and lithium ion transference number of PEO_{12}–$LiClO_4$–$Li_{0.1}Ca_{0.9}TiO_3$ NCPE are both enhanced by the addition of nanosized $Li_{0.1}Ca_{0.9}TiO_3$, with a maximum ionic conductivity of 1.02×10^{-5} S cm^{-1} at room temperature and a maximum lithium ion transference number of 0.533 at 70°C when the $Li_{0.1}Ca_{0.9}TiO_3$ content is 15 wt %. A broad electrochemical stability window suggests that the NCPE is a viable candidate for the electrolyte material in lithium polymer batteries.
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A solid-state lithium polymer battery has attracted the attention of many researchers because of its features, such as flexibility in the shape of the cell design, leak-proof electrolyte, and high safety. The key component in a solid-state lithium polymer battery is the polymer electrolyte. For a fully dried polymer electrolyte, poly(ethylene oxide) (PEO) has been considered one of the most favorable lithium conducting matrices. The main drawback of PEO-based polymer electrolytes is the relatively high crystallinity of PEO at room temperature.[1] This reduces the ionic conductivity of PEO-based polymer electrolytes to a level that is too low to satisfy the general requirements of batteries or other practical electrochemical devices. To improve the ionic conductivity at ambient temperature, most research efforts have been dedicated to obtaining solid polymer electrolyte films containing a variety of stable amorphous phases; these afford us good flexibility of the polymer chains, which favors ion transport. To date, most of the successful work has been carried out using inorganic materials, such as ceramic and nano-oxides,[2-7] layered clays,[8-10] organic–inorganic hybrid materials,[11,12] and microporous molecular sieves[13-15] as fillers to enhance the ionic conductivity of the polymer electrolytes. However, none of these inorganic fillers is an ionic conductor that introduces lithium ions into the polymer electrolyte. In an effort to further enhance the ionic conductivity, Wang et al.[16] introduced a lithium fast ionic conductor $Li_{3-2x}(Al_{1-x}Ti_x)_2(PO_4)_3$ ($x = 0.55$–1.0), produced by a conventional solid-state reaction, into a PEO-based polymer electrolyte. The ionic conductivity of a PEO–$LiClO_4$–$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ film with ethylene oxide (EO)/Li = 8 reached a maximum of 7.985 $\times 10^{-6}$ S cm^{-1} at room temperature when the $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ content was 15 wt %. However, the modal grain size of the $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ powders is larger than 0.5 μm, which may adversely affect the electrochemical properties of the resulting solid composite polymer electrolytes. Nanosized fillers have been chosen as additives in PEO-based composite polymer electrolytes and are effective in enhancing the ionic conductivity, lithium ion transference number, and electrochemical stability.[1,4] Nanosized $Li_{0.1}Ca_{0.9}TiO_3$ is a lithium fast ionic conductor just like $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$. It has a higher conductivity (4.53×10^{-4} S cm^{-1})[17] as a solid electrolyte at room temperature than that of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (10^{-5}–10^{-6} S cm^{-1}).[16] Thus, the use of nanosized $Li_{0.1}Ca_{0.9}TiO_3$ as a filler has the potential to further improve the electrochemical properties of PEO-based solid composite polymer electrolytes.

In this work, the preparation of a PEO-based solid nanocomposite polymer electrolyte (NCPE) doped with nanosized $Li_{0.1}Ca_{0.9}TiO_3$ is described. The effects of adding the nanosized $Li_{0.1}Ca_{0.9}TiO_3$ filler on the crystallinity of the PEO phase as well as on the ionic conductivity, lithium ion transference number, and electrochemical stability of the PEO-based polymer electrolyte are investigated.

Experimental

Nanosized $Li_{0.1}Ca_{0.9}TiO_3$ powders were prepared by a sol–gel method according to Ref. 17 as follows: A stoichiometric amount of $Ca(NO_3)_2 \cdot 4H_2O$ and $LiNO_3$ were dissolved in deionized water. Then, $Ti(OC_4H_9)_4$, absolute alcohol, and acetylacetone [the volume ratio employed was $Ti(OC_4H_9)_4$:absolute alcohol:acetylacetone = 4:4:1] were consecutively added dropwise into the mixture under constant stirring. After a reaction at 40°C for 4 h, a $Li_{0.1}Ca_{0.9}TiO_3$ sol was obtained. The sol was kept in an oven at 80°C for 7 days to afford the $Li_{0.1}Ca_{0.9}TiO_3$ dried gel. The final powdered product was obtained by sintering the dried gel in air at 700°C for 2 h.

PEO with a molecular weight of 100,000 and $LiClO_4$ supplied by Alfa Aesar were dried under vacuum at 50 and 100°C, respectively, for at least 48 h before use. Nanosized $Li_{0.1}Ca_{0.9}TiO_3$ powders were heated under vacuum at 150°C for 48 h to remove water before use. Films were prepared by the conventional solution cast technique as follows: Various amounts of nanosized $Li_{0.1}Ca_{0.9}TiO_3$ and PEO were dispersed in acetonitrile with the aid of ultrasonic dispersion, followed by the addition of PEO and $LiClO_4$ with a fixed [EO]/[Li] molar ratio of 12.[12,14] The solution was stirred at room temperature for 24 h until a complete homogenization of the mixture had occurred. The slurry was then cast onto a self-designed Teflon plate, and the solvent was allowed to evaporate slowly under N_2 protection at room temperature for 24 h. Finally, the samples were dried under vacuum at 50°C for 48 h and kept in an argon-filled Unilab glove box at room temperature. The films obtained were 150–200 μm thick. The NCPEs that contain $Li_{0.1}Ca_{0.9}TiO_3$ were designated as PEO_{12}–$LiClO_4 - x$ wt % $Li_{0.1}Ca_{0.9}TiO_3$, where 12 indicates the fixed [EO]/[Li] molar ratio and x denotes the amount of the nanosized $Li_{0.1}Ca_{0.9}TiO_3$ in the PEO with $x = 0$, 5, 10, 15, or 20.

X-ray diffraction (XRD) patterns of the samples were obtained by using a Shimadzu XRD-6000 diffractometer with Cu Kα radiation (40 kV and 30 mA) at a scanning rate of 5° min^{-1}.

Differential scanning calorimetry (DSC) was employed to determine the melting point (T_m) and glass transition temperature (T_g) of the polymer electrolyte using a Netzsch differential scanning calorimeter 204 F1 instrument. The measurements were carried out at a heating rate of 10°C min^{-1} from −80 to 100°C. A flow of dry nitrogen gas was maintained over the perforated pan to avoid any contact with atmospheric moisture. Sample weights were in the range of 3–5 mg, and an empty aluminum pan was used as the reference.

All IR absorption spectra were recorded on a Bruker Fourier transform IR spectrometer (model Vector 22) over the range of 4000–400 cm^{-1}. For the measurements, the mixed slurry was cast on a KBr wafer and dried via the same steps used in the preparation of the nanocomposite electrolyte films.

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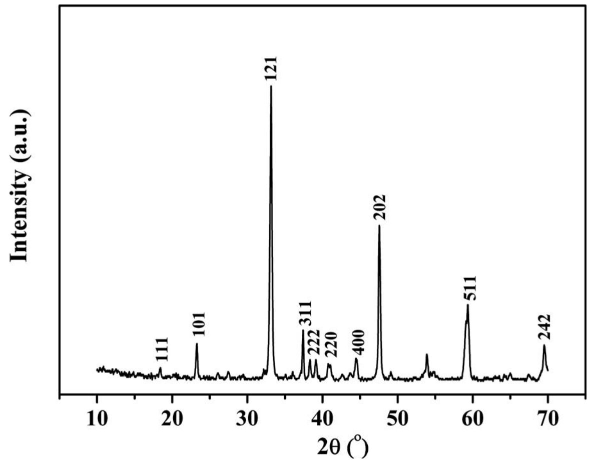

Figure 1. XRD pattern of the $Li_{0.1}Ca_{0.9}TiO_3$ powder.

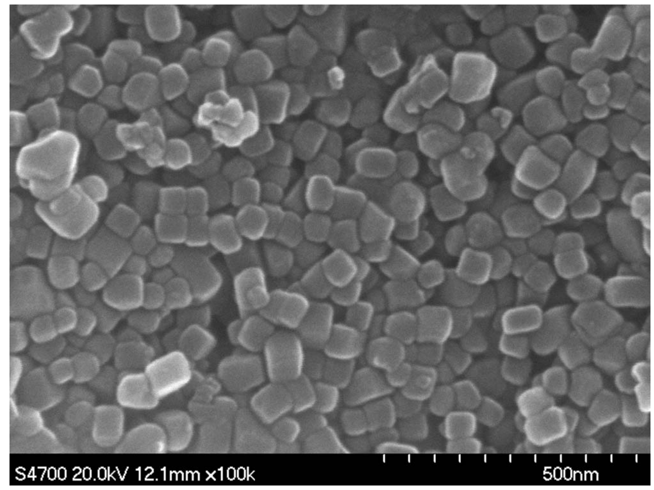

Figure 2. FESEM image of the $Li_{0.1}Ca_{0.9}TiO_3$ powder.

Sample morphologies were investigated using a Hitachi S4700 field-emission-scanning electron microscope (FESEM).

The ionic conductivity of the samples was measured using ac impedance techniques after sandwiching the samples between two stainless steel (SS) blocking electrodes, which formed an SS/NCPE/SS cell. The measurements were performed using an electrochemical workstation (IM6e, Germany) between 100 kHz and 10 Hz at various temperatures ranging from 30 to 80°C. A thermostatic bath (Julabo Labortechnik GmbH, Germany) was utilized to control the temperature to within ± 0.1°C of the target value. The samples were thermally equilibrated at each temperature for at least 2 h before the measurements. The bulk resistance (R_b) was obtained by reading the intercept of the impedance spectrum, and the ionic conductivity was calculated from the expression

$$\sigma = L/(R_b A) \quad [1]$$

where L is the thickness of the electrolyte film and A represents the electrode area.

The lithium ion transference number, T_{Li+}, was evaluated using the method of ac impedance combined with the steady-state current technique, proposed by Vincent and co-workers.[18,19] The NCPE was sandwiched between two lithium-unblocking electrodes to form a symmetrical Li/NCPE/Li cell.

The electrochemical stability window of the NCPE was determined by running a linear sweep voltammogram in three-electrode cells using SS as the working electrode and lithium as both the counter and the reference electrode. An IM6e electrochemical workstation was used with a scanning rate of 1 mV s^{-1}.

All the above-mentioned cells were assembled and sealed in an argon-filled Unilab glove box (M. Braun Ltd., Germany) ($O_2 < 1$ ppm, $H_2O < 1$ ppm).

Results and Discussion

The XRD pattern of $Li_{0.1}Ca_{0.9}TiO_3$ powder sintered at 700°C for 2 h is shown in Fig. 1. The appearance of the typical 111, 311, 400, and 222 reflection peaks indicates that $Li_{0.1}Ca_{0.9}TiO_3$ powders have crystallized well and formed a cubic perovskite structure, as suggested in the literature.[17] Figure 2 shows the FESEM image of $Li_{0.1}Ca_{0.9}TiO_3$ powder sintered at 700°C for 2 h. The powder is monodisperse, and the mean grain size is about 80 nm. These results confirm that the nanosized $Li_{0.1}Ca_{0.9}TiO_3$ powders have been prepared.

Figure 3 displays the XRD patterns of pure PEO, polymer electrolyte PEO_{12}–$LiClO_4$, and the PEO_{12}–$LiClO_4$ – 15 wt % $Li_{0.1}Ca_{0.9}TiO_3$ NCPE. The characteristic diffraction peaks of crystalline PEO are apparent between $2\theta = 15$ and 30° (Fig. 3a).[7] These diffraction peaks become broader and less prominent after the addition of $LiClO_4$ (Fig. 3b) compared with those of pure PEO, indicating a decrease in the crystallinity of PEO. The characteristic peak intensities decrease further when nanosized $Li_{0.1}Ca_{0.9}TiO_3$ is added to form the NCPEs (Fig. 3c), which confirms that nanosized $Li_{0.1}Ca_{0.9}TiO_3$ can effectively decrease the PEO crystallinity.

The glass transition temperature (T_g), melting temperature (T_m), recrystallization enthalpy (ΔH_m), and crystallinity (X_c) values of pure PEO and the polymer electrolytes PEO_{12}–$LiClO_4$ – x wt % $Li_{0.1}Ca_{0.9}TiO_3$ with $x = 0$, 5, 10, 15, and 20 are shown in Table I. Table I shows that the values of T_m and X_c both decrease when $LiClO_4$ is introduced into the PEO matrix. The values of T_m and X_c decrease further when the third component $Li_{0.1}Ca_{0.9}TiO_3$ is added to the PEO_{12}–$LiClO_4$ complex to form the NCPEs. The values of T_g, T_m, and X_c of PEO_{12}–$LiClO_4$ – x wt % $Li_{0.1}Ca_{0.9}TiO_3$ NCPEs all initially decreased markedly and subsequently increased slightly as the content of $Li_{0.1}Ca_{0.9}TiO_3$ was increased from 0 to 20 wt %. The observed decrease in T_m indicates that the addition of nanosized $Li_{0.1}Ca_{0.9}TiO_3$ can inhibit the reorganization of PEO chains effectively and hence decrease the crystallization of PEO.[7,16] The decrease in T_g indicates that the addition of nanosized $Li_{0.1}Ca_{0.9}TiO_3$ can increase the flexibility of the PEO chains.[20] This may be because the presence of $Li_xCa_{1-x}TiO_3$ perturbs the PEO chain conformation and therefore introduces additional free space

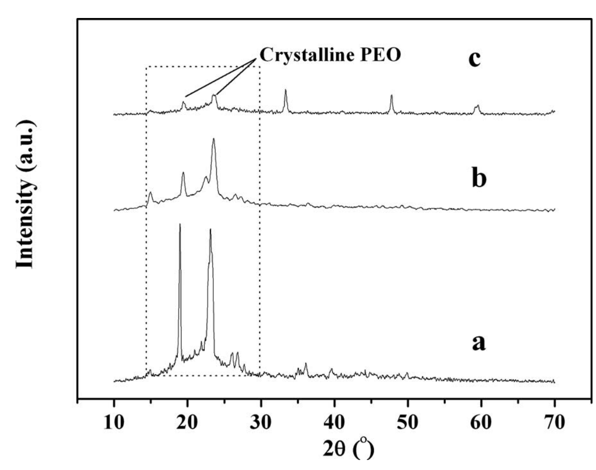

Figure 3. XRD patterns of (a) pure PEO, (b) PEO_{12}–$LiClO_4$, and (c) PEO_{12}–$LiClO_4$ – 15 wt % $Li_{0.1}Ca_{0.9}TiO_3$.

Table I. Glass transition temperature (T_g), melting temperature (T_m), recrystallization enthalpy (ΔH_m), and crystallinity (X_c) values of the polymer electrolytes PEO_{12}–$LiClO_4$ – x wt % $Li_{0.1}Ca_{0.9}TiO_3$ with x = 0, 5, 10, 15, and 20.

Sample	T_g (°C)	T_m (°C)	ΔH_m (J g^{-1})	X_c [a] (%)
Pure PEO	—	67.5	−107.1	50.12
PEO_{12}–$LiClO_4$	−19.4	64.1	−79.02	36.97
PEO_{12}–$LiClO_4$ – 5 wt % $Li_{0.1}Ca_{0.9}TiO_3$	−39.6	54.0	−31.71	14.84
PEO_{12}–$LiClO_4$ – 10 wt % $Li_{0.1}Ca_{0.9}TiO_3$	−45.5	50.7	−26.39	12.35
PEO_{12}–$LiClO_4$ – 15 wt % $Li_{0.1}Ca_{0.9}TiO_3$	−44.5	50.1	−21.95	10.27
PEO_{12}–$LiClO_4$ – 20 wt % $Li_{0.1}Ca_{0.9}TiO_3$	−42.0	51.7	−33.82	15.82

[a] $X_c = (\Delta H_m/\Delta H_m^*) \times 100$, where $\Delta H_m^* = 213.7$ J g^{-1}.[20]

between the polymer segments,[4] thus increasing PEO flexibility and lowering its T_g; this could be responsible for the enhanced ionic conductivity at a low temperature.

Figure 4 displays the IR spectra recorded for the pure PEO and PEO_{12}–$LiClO_4$ – x wt % $Li_{0.1}Ca_{0.9}TiO_3$ NCPEs with x = 0, 5, and 15. The presence of a crystalline PEO phase is confirmed by the triplet peaks of the C–O–C stretching vibrations with maxima at about 1146, 1107, and 1062 cm^{-1}.[21] In Fig. 4, we can observe that these triplet peaks become broader when Li^+ salt is added into the PEO matrix, and the intensities of the peaks become weaker after the third component $Li_{0.1}Ca_{0.9}TiO_3$ is added. This is indicative of a reduced amount of crystalline PEO, consistent with the DSC results. In the pure PEO sample, the CH_2 wagging mode peak (observed at about 1350 cm^{-1} in amorphous PEO) is split into two peaks at ~1360 and ~1343 cm^{-1}; this is further evidence for the presence of a crystalline PEO phase.[21-23] After the addition of the Li^+ salt, the two peaks at ~1360 and ~1343 cm^{-1} become broader. When the third component $Li_{0.1}Ca_{0.9}TiO_3$ is added, these two peaks disappear and only the peak at 1350 cm^{-1} can be observed. This confirms that the addition of nanosized $Li_{0.1}Ca_{0.9}TiO_3$ can effectively reduce the crystallization of PEO in PEO_{12}–$LiClO_4$ – x wt % $Li_{0.1}Ca_{0.9}TiO_3$.

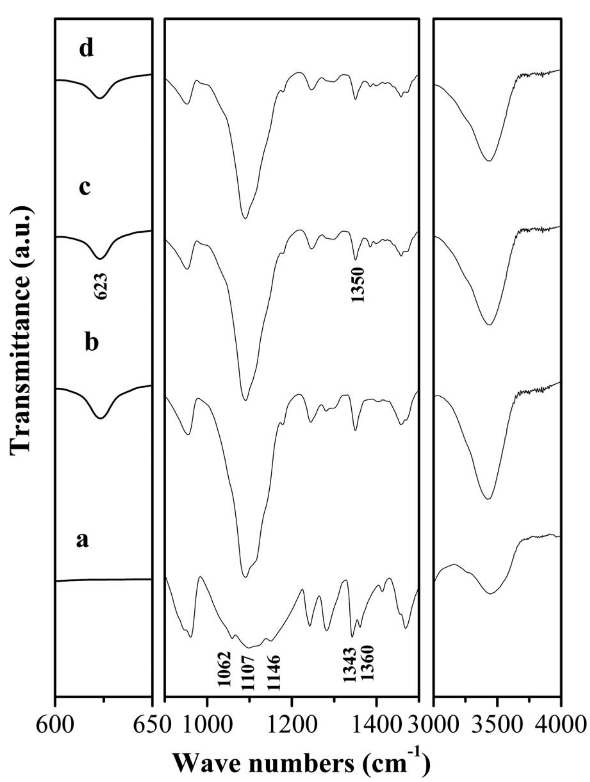

Figure 4. IR spectra of (a) pure PEO and PEO_{12}–$LiClO_4$ – x wt % $Li_{0.1}Ca_{0.9}TiO_3$ with (b) x = 0, (c) x = 5, and (d) x = 15.

The perchlorate stretching vibration peaks $\nu(ClO_4^-)$ in the region 650–600 cm^{-1} are frequently used to analyze ion–ion interactions in PEO–$LiClO_4$-based composite electrolytes. Salomon et al. suggested that the $\nu(ClO_4^-)$ band centered between 630 and 635 cm^{-1} is associated with the presence of contact-ion pairs, whereas the band centered at about 623 cm^{-1} can be attributed to free ClO_4^- anions.[21] In Fig. 4b-d, only the peak at 623 cm^{-1} characteristic of free ClO_4^- is apparent for all the PEO-based polymer electrolytes, indicating that an abundance of free Li^+ ions is present in each of these electrolytes.[21] The broader peaks characteristic of H_2O at ~3500 cm^{-1} are also observed for all the samples because exposure to moisture cannot be avoided during the preparation of the samples and the recording of the spectra.

The ionic conductivities of PEO_{12}–$LiClO_4$ – x wt % $Li_{0.1}Ca_{0.9}TiO_3$, with x = 0, 5, 10, 15, and 20 at the temperature range of 30–80°C, are shown in Fig. 5. The introduction of $Li_{0.1}Ca_{0.9}TiO_3$ powders has a marked effect on the ionic conductivity of the NCPEs. The enhancement of ionic conductivity is most pronounced at a low temperature ($<T_m$). The ionic conductivity first increases and then decreases with increasing $Li_{0.1}Ca_{0.9}TiO_3$ content. The ionic conductivity of the NCPEs reaches a maximum value of 1.02×10^{-5} S cm^{-1} at 30°C when the content of $Li_{0.1}Ca_{0.9}TiO_3$ is 15 wt %. This value is about 100 times higher than that of PEO_{12}–$LiClO_4$ at the same temperature. The enhancement of ionic conductivity of NCPEs at low temperature is mainly because the presence of nanosized $Li_{0.1}Ca_{0.9}TiO_3$ as a filler results in a larger reduction in crystallinity and more flexible local chains of PEO in the NCPE, as indicated by the reduced values of T_m and T_g. When

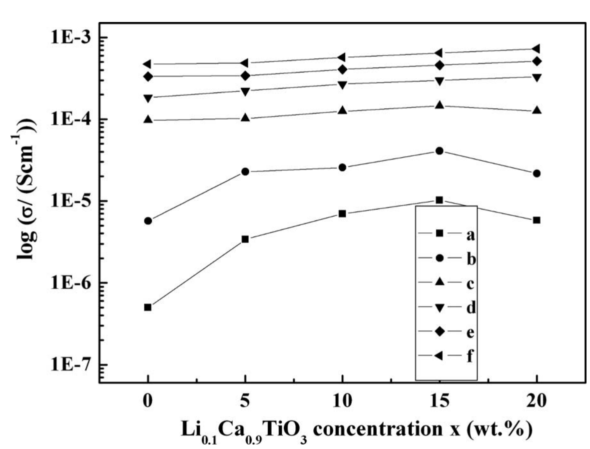

Figure 5. Dependence of the ionic conductivities of PEO_{12}–$LiClO_4$ – x wt % $Li_{0.1}Ca_{0.9}TiO_3$ NCPEs on $Li_{0.1}Ca_{0.9}TiO_3$ loading x at different temperatures: (a) 30, (b) 40, (c) 50, (d) 60, (e) 70, and (f) 80°C.

Table II. Lithium ion transference number of PEO_{12}–$LiClO_4$ – x wt % $Li_{0.1}Ca_{0.9}TiO_3$ NCPEs with x = 0, 5, 10, 15, and 20 at 70°C.

x wt %	0	5	10	15	20
Lithium ion transference number (T_{Li+})	0.242	0.384	0.471	0.533	0.457

the content of $Li_{0.1}Ca_{0.9}TiO_3$ in the NCPEs is further increased to 20 wt %, the ionic conductivity of the NCPEs decreases. This decrease in ionic conductivity can also be attributed to the change in the crystallinity of PEO in the NCPE. Because of the aggregation of $Li_{0.1}Ca_{0.9}TiO_3$ particles at relatively high loadings, the reduction in the crystallinity of PEO in the NCPE with 20 wt % $Li_{0.1}Ca_{0.9}TiO_3$ is smaller than that with 15 wt % $Li_{0.1}Ca_{0.9}TiO_3$, as indicated by the DSC results. Furthermore, the ionic conductivities of NCPEs are also higher than PEO_{12}–$LiClO_4$ at a high temperature ($>T_m$). It is possible that the presence of $Li_{0.1}Ca_{0.9}TiO_3$ itself is an important factor in enhancing the ionic conductivity of NCPE; namely, the conduction occurs not only through amorphous PEO but also within the solid state $Li_{0.1}Ca_{0.9}TiO_3$. This is suggested by the fact that at a high temperature, the ionic conductivities of the NCPEs increase with the increasing content of $Li_{0.1}Ca_{0.9}TiO_3$.

The lithium ion transference numbers (T_{Li+}) of PEO_{12}–$LiClO_4$ – x wt % $Li_{0.1}Ca_{0.9}TiO_3$ NCPEs measured at 70°C are shown in Table II. It can be seen in Table II that the T_{Li+} value of PEO_{12}–$LiClO_4$ is relatively low. A possible reason is that Li^+ can coordinate not only to the ether oxygen atoms in PEO but also to the oxygen atoms in ClO_4^-, which restricts its transport ability.[24] After the addition of $Li_{0.1}Ca_{0.9}TiO_3$, the T_{Li+} value of PEO_{12}–$LiClO_4$ – x wt % $Li_{0.1}Ca_{0.9}TiO_3$ NCPE first increases and then decreases with increasing $Li_{0.1}Ca_{0.9}TiO_3$ content from 0 to 20 wt %. The increase in T_{Li+} with the increasing content of $Li_{0.1}Ca_{0.9}TiO_3$ up to 15 wt % can be attributed to two factors: $Li_{0.1}Ca_{0.9}TiO_3$ not only complexes strongly with PEO and results in the release of more free Li^+ ions but also provides abundant free Li^+ ions in its own right. Therefore, a high concentration of mobile charge carriers in the amorphous phase results.[16] The decrease in T_{Li+} observed with the further increase in $Li_{0.1}Ca_{0.9}TiO_3$ content from 15 to 20 wt % may be due to the aggregation of $Li_{0.1}Ca_{0.9}TiO_3$ particles at relatively high loadings.

Figure 6 shows the results of linear sweep voltammetry measurements at 70°C for cells prepared with the NCPEs. In Fig. 6, we can see that PEO_{12}–$LiClO_4$–$Li_{0.1}Ca_{0.9}TiO_3$ NCPEs exhibit a good electrochemical stability [above 5.5 V (vs Li^+/Li)]. The good electrochemical stability suggests that these NCPEs are candidate electrolyte materials for rechargeable lithium polymer batteries.

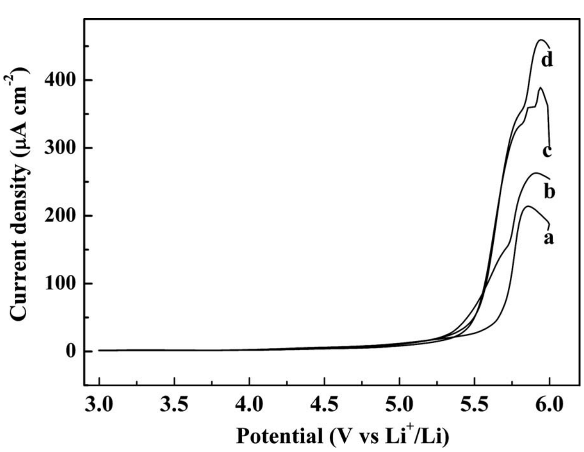

Figure 6. Current–voltage response of PEO_{12}–$LiClO_4$ – x wt % $Li_{0.1}Ca_{0.9}TiO_3$ NCPEs at 70°C on an SS electrode as the working electrode: (a) x = 5, (b) x = 10, (c) x = 15, and (d) x = 20. Scanning rate: 1 mV s^{-1}.

Conclusion

A PEO-based NCPE has been obtained by the addition of nanosized $Li_{0.1}Ca_{0.9}TiO_3$ as the filler. Analysis by XRD, DSC, and IR shows that the nanosized $Li_{0.1}Ca_{0.9}TiO_3$ can reduce the crystallization of PEO very effectively, resulting in an obvious enhancement of the ionic conductivity for PEO_{12}–$LiClO_4$–$Li_{0.1}Ca_{0.9}TiO_3$ NCPEs. The ionic conductivity of the NCPEs reaches a maximum value for a 15 wt % loading of $Li_{0.1}Ca_{0.9}TiO_3$, with a value of 1.02 $\times 10^{-5}$ S cm^{-1} at room temperature. The presence of nanosized $Li_{0.1}Ca_{0.9}TiO_3$ can also enhance the lithium ion transference number of the NCPEs. The good lithium transport properties, combined with a high decomposition voltage, suggest that PEO_{12}–$LiClO_4$–$Li_{0.1}Ca_{0.9}TiO_3$ NCPE is a viable candidate for the electrolyte material in solid-state rechargeable lithium polymer batteries.

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