A poly(ethylene oxide) (PEO)-based nanocomposite polymer electrolyte (NCPE) doped with nanosized Li$_{0.1}$Ca$_{0.9}$TiO$_3$ powder was prepared by a sol–gel method according to Ref. 17 as follows: A stoichiometric amount of Ca(NO$_3$)$_2$·4H$_2$O and LiNO$_3$ were dissolved in deionized water. Then, Ti(OCH$_3$)$_4$, absolute alcohol, and acetylacetone [the volume ratio employed was Ti(OCH$_3$)$_4$: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. 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 Nitrogen 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$_2$–LiClO$_4$–x wt % Li$_{0.1}$Ca$_{0.9}$TiO$_3$, where 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.
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

$$\sigma = L/(R_bA)$$  \hspace{1cm} [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. 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. 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 20° = 15 and 30° (Fig. 3a). 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 ($\Delta H_{rec}$), and crystallinity ($\chi$) 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 1. Table I shows that the values of $T_m$ and $\chi$ both decrease when LiClO$_4$ is introduced into the PEO matrix. The values of $T_m$ and $\chi$ 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 $T_m$, $T_g$, and $\chi$ 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. 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. This may be because the presence of $Li_{0.1}Ca_{0.9}TiO_3$ perturbs the PEO chain conformation and therefore introduces additional free space.
between the polymer segments, thus increasing PEO flexibility and lowering its $T_c$; 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 $x = 0, 5, 10, 15,$ 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$^{-1}$. In Fig. 4, we can observe that these triplet peaks become broader when Li$^+$ salt is added into the polymer matrix, and the intensities of the peaks become weaker after the addition 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 PEO$_{12}$–LiClO$_4$. The enhancement of ionic conductivity at low temperature is mainly because of an abundance of free Li$^+$ ions is present in each of these electrolytes. The broader peaks characteristic of H$_2$O at about 3600 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$_3$ powders has a marked effect on the ionic conductivity of the NCPEs. The enhancement of ionic conductivity is most pronounced at a low temperature ($T < T_m$). 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 $1.02 \times 10^{-5}$ 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 NCPEs, as indicated by the reduced values of $T_m$ and $T_c$. When 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$_3$. The perchlorate stretching vibration peaks v(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 v(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.

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. The broader peaks characteristic of H$_2$O 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 dependences 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$_3$ concentration $x$ (wt %) at different temperatures: (a) 30, (b) 40, (c) 50, (d) 60, (e) 70, and (f) 80°C.
the content of Li\textsubscript{0.1}Ca\textsubscript{0.9}TiO\textsubscript{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\textsubscript{0.1}Ca\textsubscript{0.9}TiO\textsubscript{3} particles at relatively high loadings, the reduction in the crystallinity of PEO in the NCPE with 20 wt % Li\textsubscript{0.1}Ca\textsubscript{0.9}TiO\textsubscript{3} is smaller than that with 15 wt % Li\textsubscript{0.1}Ca\textsubscript{0.9}TiO\textsubscript{3}, as indicated by the DSC results. Furthermore, the ionic conductivities of NCPEs are also higher than PEO\textsubscript{12}–LiClO\textsubscript{4} at a high temperature (\(>T_m\)). It is possible that the presence of Li\textsubscript{0.1}Ca\textsubscript{0.9}TiO\textsubscript{3} itself is an important factor in enhancing the ionic conductivity of NCPE. As a result, the conduction occurs not only through amorphous PEO but also within the solid state Li\textsubscript{0.1}Ca\textsubscript{0.9}TiO\textsubscript{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\textsubscript{0.1}Ca\textsubscript{0.9}TiO\textsubscript{3}.

The lithium ion transference numbers (\(T_{Li^+}\)) of PEO\textsubscript{12}–LiClO\textsubscript{4} – x wt % Li\textsubscript{0.1}Ca\textsubscript{0.9}TiO\textsubscript{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\textsubscript{12}–LiClO\textsubscript{4} is relatively low. A possible reason is that Li\textsuperscript{+} can coordinate not only to the ether oxygen atoms in PEO but also to the oxygen atoms in ClO\textsubscript{4}\textsuperscript{−}, which restricts its transport ability.\textsuperscript{28} After the addition of Li\textsubscript{0.1}Ca\textsubscript{0.9}TiO\textsubscript{3}, the \(T_{Li^+}\) value of PEO\textsubscript{12}–LiClO\textsubscript{4} – x wt % Li\textsubscript{0.1}Ca\textsubscript{0.9}TiO\textsubscript{3} NCPE first increases and then decreases with increasing Li\textsubscript{0.1}Ca\textsubscript{0.9}TiO\textsubscript{3} content from 0 to 20 wt %. The increase in \(T_{Li^+}\) with the increasing content of Li\textsubscript{0.1}Ca\textsubscript{0.9}TiO\textsubscript{3} up to 15 wt % can be attributed to two factors: Li\textsubscript{0.1}Ca\textsubscript{0.9}TiO\textsubscript{3} not only complexed strongly with PEO and results in the release of more free Li\textsuperscript{+} ions but also provides abundant free Li\textsuperscript{+} ions in its own right. Therefore, a high concentration of mobile charge carriers in the amorphous phase results.\textsuperscript{16} The decrease in \(T_{Li^+}\), observed with the further increase in Li\textsubscript{0.1}Ca\textsubscript{0.9}TiO\textsubscript{3} content from 15 to 20 wt % may be due to the aggregation of Li\textsubscript{0.1}Ca\textsubscript{0.9}TiO\textsubscript{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\textsubscript{12}–LiClO\textsubscript{4}–Li\textsubscript{0.1}Ca\textsubscript{0.9}TiO\textsubscript{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.

### Table II. Lithium ion transference number of PEO\textsubscript{12}–LiClO\textsubscript{4} – x wt % Li\textsubscript{0.1}Ca\textsubscript{0.9}TiO\textsubscript{3} NCPEs with x = 0, 5, 10, 15, and 20 at 70°C.

<table>
<thead>
<tr>
<th>x wt %</th>
<th>Lithium ion transference number ((T_{Li^+}))</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>0.242</td>
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<tr>
<td>5</td>
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<td>15</td>
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<tr>
<td>20</td>
<td>0.457</td>
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### References