

Silver ion conducting nanocomposite polymer electrolytes: Ion transport and battery fabrication

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Ion transport characterization studies on a new Ag⁺ ion conducting (poly-ethylene oxide) PEO-based nanocomposite electrolytes (NCPEs): (1-x) [30PEO:70(0.75AgI:0.25AgCl)] + x SiO₂, where 0 < x < 20 wt.%, have been reported. A novel hot-press/ solvent free technique has been used for the formation of the present NCPE films. Nano-size (~ 8 nm) SiO₂ particles have been dispersed as a second dispersoid in to the first phase host matrix: [30PEO:70(0.75AgI:0.25AgCl)], identified as the highest conducting polymer electrolyte composition. A conductivity enhancement of more two orders that of the pure polymer-electrolyte host could be achieved in the nano-composite polymer electrolyte composition: 95[30PEO:70(0.75AgI:0.25AgCl)] + 5SiO₂ ($\sigma \sim 6.2 \times 10^{-5} \text{ S.cm}^{-1}$) and this has been referred to as optimum conducting composition (OCC). Polymer-salt/ nano-filler complexations have been explained with the help of XRD, DSC and TGA analysis. To explain the ion transport characterization various ionic transport parameters viz. conductivity (σ), ionic mobility (μ), mobile ion concentration (n), ionic transference number (t_{ion}) etc. have been determined at room temperature and the temperature dependent conductivity measurements have also been carried out to evaluate the activation energy (E_a). A new Ag⁺ ion conducting solid state polymer battery have been fabricated and studied the cell parameters at room temperature.

Keywords: Nanocomposite polymer electrolytes, Ionic conductivity, Ionic transference number, DSC, TGA, Polymer battery

1 Introduction

The development of a new ion conducting superionic solids shows great technological promises as potential electrolyte systems to fabricate all solid-state electrochemical devices viz. batteries, fuel cells, super-capacitors, memories electrochromic displays etc¹⁻³. In the last 3-4 decades, a large number of solid state ionic materials in different phases such as crystalline/ polycrystalline, glassy/ amorphous, composite, ceramic, polymeric etc. and involving variety of mobile ionic species viz. H⁺, Li⁺, Ag⁺, Cu⁺, Na⁺, F⁻, O²⁻ etc. has been discovered. Their technological feasibilities in the solid state electrochemical device applications are constantly being explored. Amongst the known superionic solids, polymeric electrolyte systems, including conventional, micro/ nano composite/ gels, attracted widespread attention as the most appropriate choice to fabricate flexible, compact laminated all-solid-state electrochemical batteries⁴⁻¹². Polymer electrolytes are prepared, in general, by complexing ionic salts in variety of polymeric hosts by dissolving both the salt

and polymer in a common solvent. Majority of the polymer electrolyte films discovered so far, are either alkali ion (Li⁺, Na⁺) or proton conducting systems. There are very few systems reported which involve other mobile ions viz. Ag⁺, Cu⁺ etc. This is probably due to the limitation of the preparation technique based on solution-cast. In the present paper, a novel hot-press technique has been reported for casting polymer electrolyte membranes. This is a more rapid and least expensive solvent-free procedure to form completely dry polymer electrolyte membranes complexed with variety of ionic salts¹³⁻¹⁷.

The present paper reports the synthesis of a new Ag⁺ ion conducting nanocomposite polymer electrolytes (NCPEs): (1-x) [30PEO:70(0.75AgI:0.25AgCl)] + x SiO₂, where 0 < x < 20 wt.%, using hot-press/ dry method. To explain ion conductance behavior of the present NCPEs, various ion transport parameters viz. conductivity (σ), ionic mobility (μ), mobile ion concentration (n), ionic transference number (t_{ion}) etc. measured experimentally employing different techniques. A solid state polymer battery is also fabricated by using the present NCPE.

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2 Experimental

A new Ag^+ ion conducting nanocomposite polymer electrolytes (NCPEs): $(1-x)$ [30PEO:70 (0.75AgI:0.25AgCl)] + x SiO_2 , where $0 < x < 20$ wt.%, were prepared by hot-pressing the dry powder mixtures of AR grade chemicals: poly (ethylene oxide) PEO (10^5 MW, Aldrich, USA), AgI and AgCl (purity > 98%, Reidel, India), SiO_2 (> 99.8%, size ~ 8 nm, Sigma, USA). Firstly the host polymer electrolyte: [30PEO:70(0.75AgI:0.25AgCl)] have been synthesized in hot-press method, as mentioned in our previous communication¹⁸. To prepare the present NCPEs, the dry powders of host polymer was homogeneously mixed with different wt.% ratios of SiO_2 , heated ~80 °C to form slurry, then hot-pressed between SS blocks resulting finally into a mechanically stable films.

Polymer-salt/ filler SiO_2 complexation and materials characterization were done with the help of X-ray diffraction (XRD) patterns (model: Shimadzu X-ray diffractometer), scanning electron microscopy (SEM) (model: JEOL, JXA-8100, Japan), differential scanning calorimetry (DSC) (model: Perkin Elmer) and thermogravimetric analysis (TGA) (model: SDT Universal).

The ionic conductivity (σ) measurements were carried out by using an LCR-bridge (HIOKI 3520 - 01, Japan) with the help of following equation:

$$\sigma = \frac{l}{R_b \cdot A} \quad \dots (1)$$

where R_b is the bulk resistance, l is the thickness and A is the cross sectional area of the polymeric sample material. The bulk resistance R_b was determined from the impedance analysis by using an LCR- bridge (model: HIOKI 3520- 01, Japan). The ionic mobility (μ) and ionic transference number (t_{ion}) were also determined by using transient ionic current (TIC) technique with the help of following equations^{19,20}:

$$\mu = \frac{d^2}{V \cdot \tau} \quad \dots (2)$$

and

$$t_{\text{ion}} = 1 - \frac{I_e}{I_T} \quad \dots (3)$$

where I_e is the electronic current and I_T is the total current of the cell: [SS // NCPE OCC // SS]. Subsequently, the mobile ion concentrations were also determined from the well-known relation: $\sigma = n \cdot q \cdot \mu$.

Temperature dependent conductivity was done on SPE host and OCC membranes to evaluate the activation energy (E_a) values. A new solid state polymer battery is fabricated by using the highest conducting composition of the present NCPE as an electrolyte.

3 Results and Discussion

3.1 Ion transport characterization

Figure 1 shows the nano filler SiO_2 -concentration dependent conductivity plot for a new Ag^+ ion conducting nanocomposite polymer electrolytes (NCPEs): $(1-x)$ [30PEO:70(0.75AgI:0.25AgCl)] + x SiO_2 at room temperature. The conductivity (σ) of the host polymer electrolyte [30PEO:70 (0.75AgI:0.25AgCl)] increases with the SiO_2 concentrations and a maxima in conductivity ($\sigma \sim 6.2 \times 10^{-5} \text{ S.cm}^{-1}$) was obtained at 5 wt.% SiO_2 . On further addition of SiO_2 , ' σ ' dropped to a much lower value. Two orders of conductivity enhancement have been achieved for the nanocomposite polymer electrolyte composition: 95[30PEO:70(0.75AgI:0.25AgCl)] + 5 SiO_2 . The mechanical strength of the nanocomposite polymer electrolyte film was observed to be substantially enhanced from that of the undispersed films. This composition has been referred to as the Optimum Conducting Composition (OCC).

The conductivity variation of this kind has invariably been witnessed in majority of 2-phase inorganic composite electrolytes and the mechanism of conductivity enhancements in these systems could

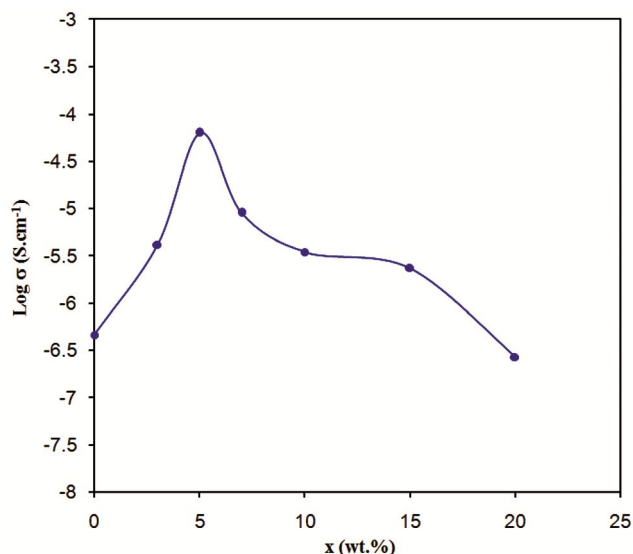


Fig. 1 – 'Log σ -x' plot for the NCPEs: $(1-x)$ [30PEO:70(0.75AgI:0.25AgCl)] + x SiO_2 , where $0 < x < 20$ wt.%.

by understood by various proposed models which are principally based on space-charge double layer effect^{21,22}. The dispersal of submicron size filler particles, containing large surface area, into the solid polymer electrolyte host additionally creates a high degree of amorphousity and/ or lowers the degree of crystallinity which may also be thought to be due to Lewis-acid-base interaction between ceramic surface states and polymer segments^{23,24}.

The increase in ionic conductivity in NCPE OCC is due to the increase in degree of amorphicity. To characterize the another reason of ion conductance behavior of this OCC film, the ionic mobility (μ), mobile ion concentration (n) and ionic transference number (t_{ion}) were determined employing a dc polarization TIC- technique, as mentioned in Experimental Section. Figure 2 shows 'log μ - x ' and 'log n - x ' plots for NCPEs: $(1-x)$ [30PEO:70 (0.75AgI:0.25AgCl)] + x SiO₂ at room temperature. It is obvious from the figure that the increase in room temperature conductivity of the present NCPE OCC is due to the increase in both μ and n and this is due to the available of more numbers of mobile Ag⁺ ions and free

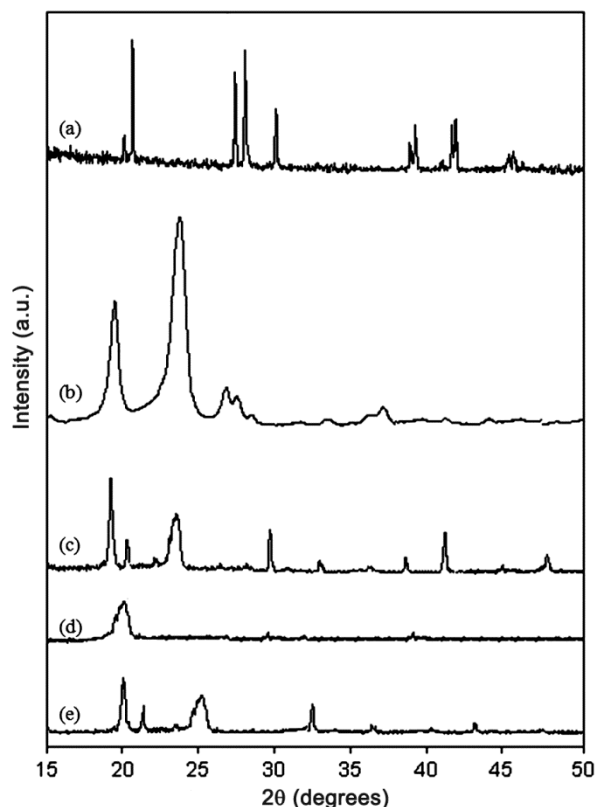


Fig. 2 – XRD patterns: (a) (0.75AgI:0.25AgCl), (b) pure PEO, (c) SPE host: [70PEO: 30(0.75AgI:0.25AgCl)], (d) SiO₂ and (e) NCPE OCC: 95 [70PEO:30(0.75AgI:0.25AgCl)] + 5 SiO₂.

conduction paths in the system as well as increase in 'n' is due to the space charge double layer effect^{25,26}. The ionic transference number (t_{ion}) of SPE host and NCPE OCC has been evaluated using dc polarization TIC technique, as mentioned in Section 2. $t_{ion} \sim 0.9$ obtained for both the films and it is clearly confirms the present NCPE is a pure ion conducting system with 90% Ag⁺ ions are mobile in the system and only a small contribution of anions.

In order to confirm the salt complexation in the polymeric electrolyte host, X-ray diffraction analysis was done on NCPE OCC, SPE host, SiO₂ and pure PEO materials and the diffraction patterns are shown in Fig. 2. On a closer inspection, it can be noted that some of the peaks of pure PEO became relatively broader as well as less-prominent/ feeble after salt complexation/ SiO₂ dispersal. This is usually attributed to the increase (decrease) in the degree of amorphousity (crystallinity) and also confirmed the salt complexation as well as to some extent, dispersal of nano-SiO₂ in the polymeric host. However, the characteristic peaks belonging to AgI and SiO₂ could not be noticed distinctly in the XRD pattern which may probably be due to their presence in the relatively low percentage in the system as compared to PEO and/ or overlapping of some of their main peaks with those of PEO.

Figure 3 shows the surface morphology of SPE host and NCPE OCC were observed by scanning electron micrograph (SEM). It can be clearly seen from the figure that the NCPE OCC shows the smooth surface morphology while the pure PEO shown the rough morphology. It is closely related to the reduction of crystallinity, as mentioned elsewhere²⁷⁻³¹.

Figure 4 shows the DSC thermograms for the pure PEO, SPE host: 30PEO:70(0.75AgI:0.25AgCl) and NCPE OCC: 95 [30PEO:70(0.75AgI:0.25AgCl)] + 5 SiO₂. The broad endothermic peak was observed in polymeric films at ~ 60 -70 °C and it is

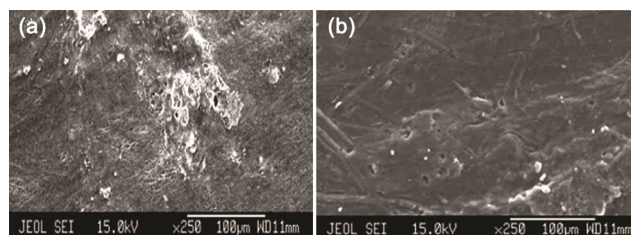


Fig. 3 – SEM images: (a) SPE host: [70PEO: 30(0.75AgI:0.25AgCl)], and (b) NCPE OCC: 95 [70PEO: 30(0.75AgI:0.25AgCl)] + 5 SiO₂.

corresponding to the melting point temperature of pure PEO. It is clearly shown from the figure that the melting temperature (T_m) of pure PEO decreased from 70 °C to 67 °C, due to the increase in degree of amorphicity in SPE host and again decreased the T_m in NCPE OCC (63 °C). It is due to the interaction between the PEO backbone and the filler SiO_2 have affected the main chain dynamics of the SPE host. A possible mechanism for this behavior could be the creation of additional hopping sites and favorable conducting pathways for ionic migration³²⁻³⁴.

Figure 5 shows the thermogravimetric analysis (TGA) curves pure PEO, SPE host:

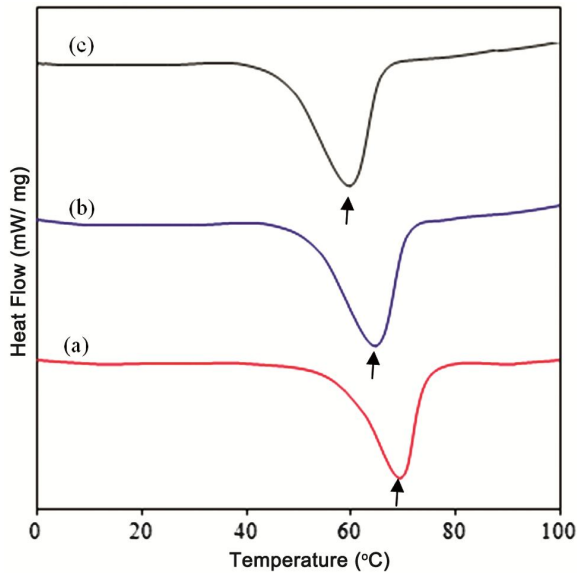


Fig. 4 – DSC thermograms: (a) pure PEO, (b) SPE host: [70PEO: 30(0.75AgI:0.25AgCl)] and (c) NCPE OCC: 95 [70PEO:30(0.75AgI:0.25AgCl)] + 5 SiO₂.

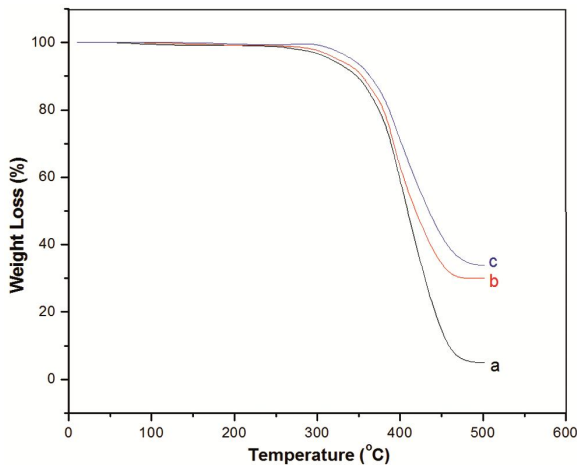


Fig. 5 – TGA curves: (a) pure PEO, (b) SPE host: [70PEO: 30(0.75AgI:0.25AgCl)] and (c) NCPE OCC: 95 [70PEO:30(0.75AgI:0.25AgCl)] + 5 SiO₂.

30PEO:70(0.75AgI:0.25AgCl) and NCPE OCC: 95 [30PEO:70(0.75AgI:0.25AgCl)] + 5 SiO₂. It can be clearly observed from the figure that the total weight loss for pure PEO (~ 95 %) is larger as compared to both SPE host (~ 70 %) and NCPE OCC (~ 66 %). The thermal stability of polymer is improved and degree of amorphicity is also increases by the dispersal of nano-filler SiO₂.

Figure 6 shows the temperature dependent conductivity variations for the SPE host: 30PEO:70(0.75AgI:0.25AgCl) and NCPE OCC: 95 [30PEO:70(0.75AgI:0.25AgCl)] + 5 SiO₂. Below the transition temperature (region-I), the equations, governing the straight line portion of Arrhenius plots ‘log σ - 1/T’ for SPE host and NCPE OCC films, can be expressed as:

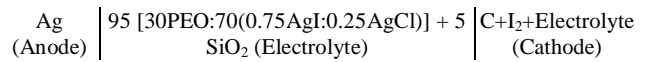
$$\text{SPE host : } \sigma(T) = 1.4 \times 10^{-3} \exp(-0.45/kT) \quad \dots (4)$$

$$\text{NCPE OCC: } \sigma(T) = 2.9 \times 10^{-4} \exp[-0.31/kT] \quad \dots (5)$$

where $E_a = 0.45$ and 0.31 eV are the activation energy values (listed in Table 1) for SPE host and NCPE OCC respectively. The lower E_a -value of NCPE OCC as compared to the host polymer is indicative of an easy ion migration within the bulk in the present NCPE system.

3.2 Battery fabrication

A new Ag⁺ ion conducting solid state polymeric battery was fabricated in the following cell configuration:



Ag-metal was used as anode while cathode film was prepared by hot-pressing the homogeneous

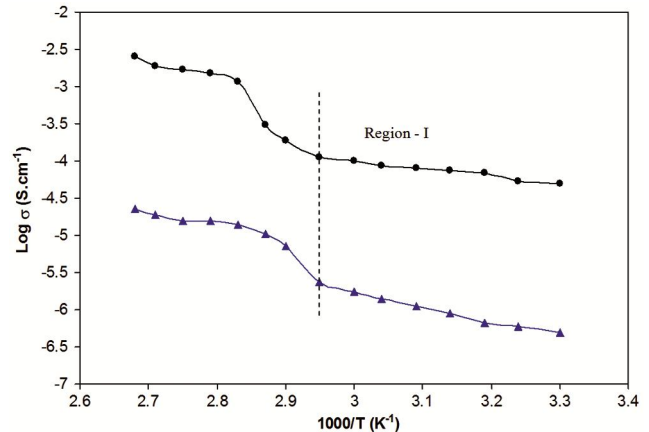


Fig. 6 – ‘Log σ -1/T’ Arrhenius plot for the Ag⁺ ion conducting nano-composite polymer electrolyte OCC: 95 [30PEO: 70(0.75AgI:0.25AgCl)] + 5 SiO₂.

Table 1 – Some important ionic parameters of the host polymer, NCPE OCC and pure PEO films.

System	$\sigma_{27}^{\circ C}$ (Scm^{-1})	$\mu_{27}^{\circ C}$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	$n_{27}^{\circ C}$ (cm^{-3})	E_a (eV)	t_{ion}
Pure Polymer: PEO	3.2×10^{-9}	-	-	-	-
Host Polymer: [70PEO:30(0.75AgI:0.25AgCl)]	4.5×10^{-7}	2.4×10^{-3}	1.5×10^{15}	0.45	0.9
NCPE OCC: 95 [70PEO:30(0.75AgI:0.25AgCl)] + 5 SiO ₂	6.2×10^{-5}	7.7×10^{-3}	9.33×10^{15}	0.31	0.9

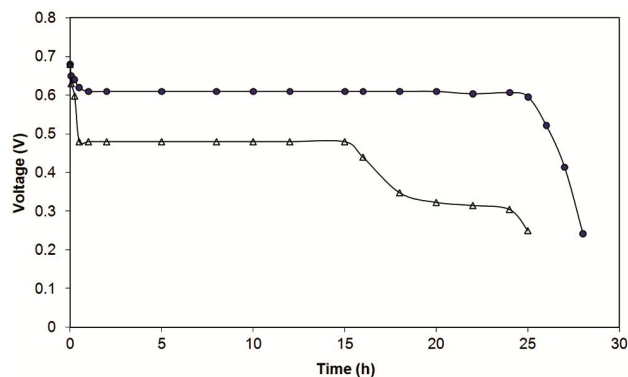


Fig. 7 – Cell potential discharge profiles of solid state polymer battery at room temperature under different load resistances: 50 (Δ) and 100 (\bullet) k Ω .

physical mixture of elemental iodine (I_2), conducting graphite (C) and NCPE in 1:1:1 weight ratios at 50 $^{\circ}\text{C}$.

Figure 7 shows the cell potential discharge profiles of the solid state battery under 50 and 100 k Ω loads at room temperature. The open circuit voltage (OCV) \sim 0.68 V obtained for the polymeric cells. The initial sharp decrease in voltage of these thin film solid-state batteries may be due to the initial cell polarization effect and/ or the formation of a thin layer of salt at the electrode/ electrolyte interface³⁵⁻³⁷. It can be clearly noticed that except for the initial potential drop, OCV value remains practically stable for \sim 25 and \sim 15 h. When discharged through 100 & 50 k Ω , respectively, (i.e., during a low current drain state). However, the cell potential decreases relatively faster when discharged through 50 k Ω load (i.e., during higher current drain states). A good performance at higher current rate may be ascribed to the efficient ionic conduction in the polymer separator and also the favorable interfacial charge transport between electrodes and electrolyte in the cell. Table 2 lists some important cell parameters for the present polymeric cell, calculated in the plateau regions of the discharge profiles. On the basis of these studies, it can be observed that the performance of the present battery have been relatively better at high load resistance or during low current drain states.

Table 2 – Some important battery parameters calculated in the plateau regions of the discharge profiles.

Load (k Ω)	Working voltage (V)	Current density ($\mu\text{A}\cdot\text{cm}^{-2}$)	Discharge capacity ($\mu\text{A}\cdot\text{h}$)	Power density ($\text{mW}\cdot\text{kg}^{-1}$)	Energy density ($\text{mWh}\cdot\text{kg}^{-1}$)
100	0.61	0.594	66.78	0.108	11.34
50	0.48	0.519	41.7	0.090	6.81

4 Conclusions

A new Ag^+ ion conducting nanocomposite polymer electrolyte: 95 [30PEO:70(0.75AgI:0.25AgCl)] + 5 SiO₂ (wt.%) has been prepared using a hot-press/ dry method. Dispersal of nano- SiO₂ particles into the polymer electrolyte host resulted into an enhancement in the room temperature conductivity. Materials characterization and polymer-salt complexation have been done by using XRD, SEM, DSC and TGA techniques. The ion transport characterizations have been explained with the help of ' μ ', ' n ' and ' t_{ion} ' measurements. Ionic mobility and mobile ion concentration both are responsible for conductivity enhancement in the present system. $t_{\text{ion}} \simeq 0.9$ is indicative of the fact that the 90% of Ag^+ ions are mobile in the present system and only a negligible contribution of electronic conduction. A new silver ion conducting solid state polymer battery was fabricated and the cell potential discharge characteristics have been studied under varying load conditions. The cell performed fairly satisfactorily under low current drain states.

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