

SYNTHESIS, CHARACTERIZATION AND ION TRANSPORT PROPERTIES OF HOT-PRESSED SOLID POLYMER ELECTROLYTES (1-*x*) PEO:*x* KI*

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Abstract Synthesis and ion transport properties of hot-pressed solid polymer electrolytes (SPEs), (1-*x*) PEO: *x* KI, where *x* is the content of KI in wt%, are reported. A hot-press technique has been used for the formation of the polymeric membranes in place of the usual solution cast method. The composition (80 PEO:20 KI) was identified as the highest conducting polymer electrolyte on the basis of compositional dependent conductivity studies of PEO:KI films. A conductivity enhancement of more than two orders of magnitude from that of the pure PEO was achieved. Materials characterization and ion transport mechanism were explained by using various experimental techniques.

Keywords: Solid polymer electrolyte; Hot-press technique; Ionic conductivity; Ionic mobility; XRD; Polymeric battery.

INTRODUCTION

Superionic materials are new class of solid systems which exhibit high ionic conductivity comparable to liquid/aqueous electrolytes^[1–6]. These materials show great technological promises as potential electrolyte systems to fabricate all solid-state electrochemical devices *viz.* batteries, fuel cells, super-capacitors, memories electrochromic displays *etc.* In the last 3–4 decades, a large number of superionic materials in different phases, such as crystalline/polycrystalline, glassy/amorphous, composite, ceramic, polymeric *etc.* involving variety of mobile ionic species *viz.* H⁺, Li⁺, Ag⁺, Cu⁺, Na⁺, K⁺, 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 batteries^[7–19]. Pure PEO has a poor conductivity (*ca.* 10⁻⁹ S/cm) at room temperature but the conductivity can be improved substantially by incorporating salts into the polymer^[11, 12, 18]. Polymer-salt complexation provides mobile ions and the polymer host chains play a critical role in ionic transport process of the polymer electrolytes. Ion transport occurs through amorphous regions assisted by the segmental motion of the polymer chains. Polymer electrolytes are prepared, in general, by complexing ionic salts in variety of polymeric hosts by dissolving both the salt and the 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⁺, K⁺ *etc.* This is probably due to the limitation of the preparation technique based on solution-cast. Recently, several workers synthesized a number

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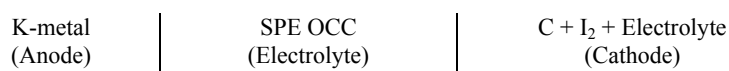
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of solid polymer electrolytes (SPEs) and nano-composite polymer electrolytes (NCPEs): (PEO:LiCF₃SO₃:Al₂O₃)^[15], (PEO:NH₄HSO₄:SiO₂)^[16], (PEO:NaPO₃)^[17], (PEO:KNO₃:SiO₂)^[18], (PEO:LiCF₃SO₃:MMT)^[19] etc. by hot-press technique over the conventional solution-cast method. They found that the hot-press method shows a number of merits over the conventional solution-cast method. This technique is more rapid, less expensive and solvent-free. Among the known alkali salts, KI is available in low cost as well as this can be potentially used for industrial applications as they are corrosive and cost matter^[20]. In the present paper, we report the synthesis and ion transport properties of a PEO-based solid polymer electrolyte system: (PEO-KI) using hot-press-dry technique. The polymer-salt complexation and morphology are studied through XRD, FTIR, DSC and SEM analysis. Solid state polymer batteries have been fabricated using the hot-press synthesized SPE.

EXPERIMENTAL

As supplied chemicals: poly(ethylene oxide) PEO (10⁵ M_w, Aldrich, USA) and KI (purity > 98%, Merck, India) have been used for synthesis of hot-pressed solid polymer electrolytes (SPEs), (1-*x*) PEO:*x* KI where 0 < *x* < 50 wt%. These SPEs were prepared by using a hot-pressed method in place of the traditional solution-cast technique. For synthesis of hot-press SPEs, dry powders of KI as complexing salts and poly(ethylene oxide) PEO as polymeric host in different ratios were ground thoroughly at room temperature for about *ca.* 1 h in an agate pestle and mortar. The physically mixed PEO-salt mixtures of different compositions were heated separately close to the melting point of PEO (*ca.* 70°C) for *ca.* 30 min with mixing continuing. This resulted in a hot/soft slurry of polymer complexed with the salt. The slurry so obtained was then pressed between two SS-cold blocks at *ca.* 1.25 ton cm⁻² which gave rise to a uniform thin membrane of thickness *ca.* 0.014 cm. All these operations were done at room temperature, as reported in our earlier communications^[17, 21, 22]. Polymer-salt complexation and materials characterization were done with the help of XRD patterns using a Shimadzu X-ray diffractometer at Cu-Kα radiation and FTIR (model: Shimadzu-8400). SEM (model: JEOL, JXA-8100, Japan) has been used to study the surface morphology only on the hot-pressed SPE OCC film. The structural and thermal studies were done with the help of differential scanning calorimetry (DSC) [model: Perkin Elmer]. The conductivity (σ)-measurements were carried out by the equation $[\sigma = l/(R_b \cdot A)]$, 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 on different polymeric samples at a fixed frequency (*i.e.* 5 kHz) using an LCR-bridge (model: HIOKI 3520-01, Japan). The ionic mobility was determined with the help of a well-known equation $[\mu = d^2/(V \cdot \tau)]$, where *d* is the thickness of SPE films, *V* is the applied external d.c. potential and *τ* is the time of flight. The time of flight (*τ*) was determined directly by employing the dc polarization Transient Ionic Current (TIC) technique using an *x-y-t* recorder (model: Graphtec WX 2300-1L, Japan)^[23, 24]. The mobile ion concentration (*n*) was evaluated from σ and μ data by using the well-known relation ($\sigma = n q \mu$). To determine the activation energy (*E_a*) values of SPE host and NCPEs the temperature dependent conductivity studies were done. Solid state polymer batteries were fabricated in the following cell configuration:



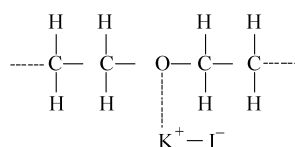
The cell performances were studied under different load conditions at different temperatures. The cell potential discharge profiles were drawn as a function of time and some important cell parameters were calculated from the plateau of the discharge profiles.

RESULTS AND DISCUSSION

Ion Transport Parameters and Materials Characterization

The room temperature compositional dependent conductivity (σ) variation as a function of salt KI concentration for the hot-pressed solid polymer electrolytes (SPEs), (1-*x*) PEO:*x* KI, is shown in Fig. 1. The room temperature

conductivity increased initially with the increase of the salt (KI) concentration in the pure polymer PEO. The conductivity (σ) maxima were observed at 20 wt% of KI *i.e.* the composition (80 PEO:20 KI) and then decreased gradually. This highest conducting composition is known as the optimum conducting composition (OCC). The increase in conductivity is due to the increase in degree of amorphicity and the creation of additional hopping sites as well as the availability of more mobile ions in the polymer network. The decrease in room temperature conductivity is due to the ion-ion association (pairing) effect. The ionic mobility (μ) and mobile ion concentration (n) of SPEs were determined directly at room temperature using dc polarization TIC technique, as mentioned in Section EXPERIMENTAL. Figure 2 shows $\lg\mu$ - x and $\lg n$ - x plots for SPEs, (1- x) PEO: x KI. It is obvious from the figure that the increase in room temperature conductivity of SPE OCC is due to the increase of mobile K^+ ions in the system. The room temperature values of some of the ionic parameters σ , μ , n and E_a are listed in Table 1. Figure 3 shows the X-ray diffraction patterns for the pure PEO, salt KI and hot-pressed SPE OCC (80 PEO:20 KI). One can clearly observe in XRD diffractograms for hot-pressed SPE OCC the characteristic peaks of pure PEO are found to shift at some peak positions and to have less prominent/variations in the peak intensities, and it is due to the decrease in degree of crystallinity. It is well-known that such features occurring in XRD pattern, give clear indication of the polymer-salt complexation. To confirm the complexation between polymer PEO and salts KI a powerful FTIR technique was used, as mentioned in Section EXPERIMENTAL. Figure 4 shows the FTIR spectra for the pure PEO, KI and hot-pressed SPE OCC (80 PEO:20 KI). The possible configuration of newly hot-pressed SPE OCC is shown in Scheme 1.



Scheme 1 A schematic presentation of cross-linking process in polymer (PEO) with salt (KI)

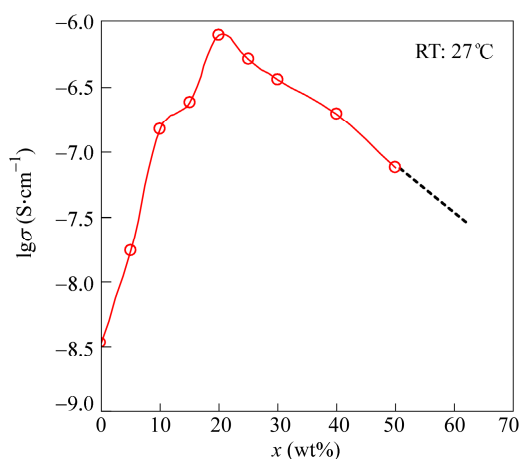


Fig. 1 Compositional dependent conductivity plot of hot-pressed SPE films (1- x) PEO: x KI

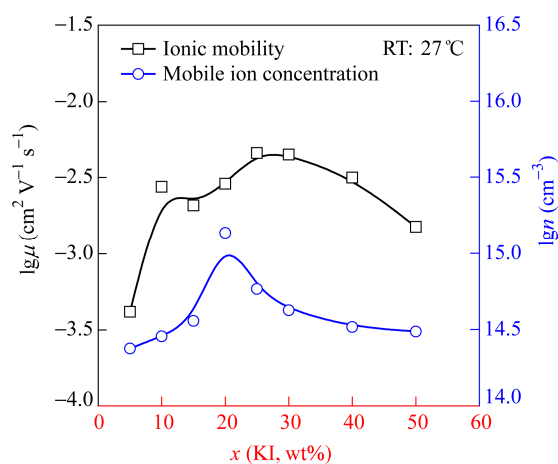


Fig. 2 Compositional dependent mobility and mobile ion concentration plots of hot-pressed SPE films (1- x) PEO: x KI

Table 1. Some important ionic parameters of SPE OCC and pure PEO at room temperature

Systems	σ (S/cm)	μ (cm ² V ⁻¹ s ⁻¹)	n (cm ⁻³)	E_a (eV)
Pure PEO	3.2×10^{-9}	—	—	—
SPE OCC (80 PEO:20 KI)	6.3×10^{-7}	2.85×10^{-3}	1.38×10^{15}	0.36

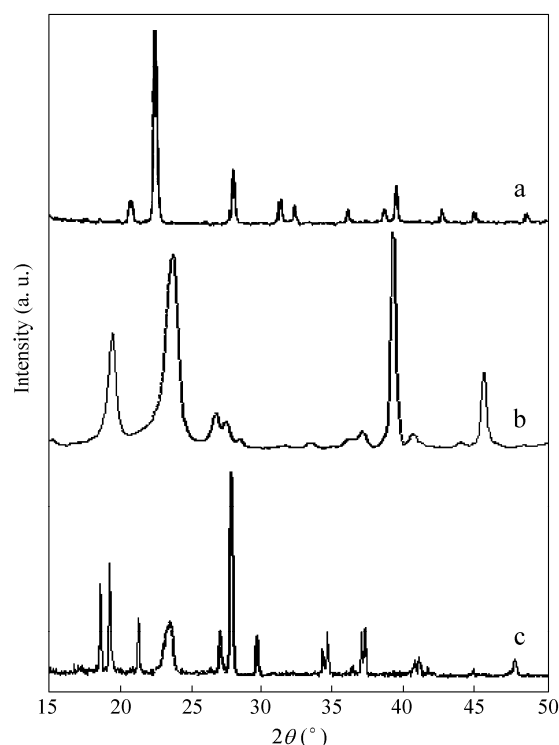


Fig. 3 XRD patterns of (a) pure PEO, (b) KI and (c) hot-pressed SPE OCC film (80 PEO:20 KI)

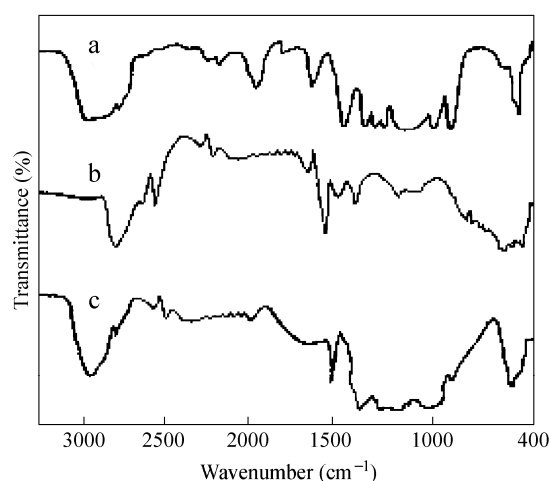


Fig. 4 FTIR spectra of (a) PEO, (b) KI and (c) hot-pressed SPE OCC film (80 PEO:20 KI)

The most important absorption features present in PEO are CH_2 bending at 1466 cm^{-1} , $\text{C}-\text{C}$ stretching at 1147 cm^{-1} , $\text{C}-\text{O}-\text{C}$ asymmetric stretching at 962 cm^{-1} and CH_2 asymmetric rocking at 843 cm^{-1} . It is clearly indicated from the spectra that the width of the $\text{C}-\text{O}-\text{C}$ and $\text{C}-\text{H}$ stretching modes decreases after addition of salts at *ca.* 1100 cm^{-1} and *ca.* 2900 cm^{-1} respectively and the peaks at *ca.* 820 cm^{-1} broaden. All these results and symmetrical and asymmetrical changes in vibrational bands with ether oxygen, indicate that complexation of KI with PEO takes place, and such type of interesting behavior with alkali salts was also suggested in the literature^[25–28]. Figure 5 shows the surface morphology of SPE OCC (80 PEO:20 KI) and clearly indicates an almost smooth surface. It is also closely related to the enhancement of amorphicity with KI salt, while pure PEO

usually shows a rough morphology^[29]. DSC thermograms for the pure PEO and hot-pressed SPE OCC are shown in Fig. 6. It can be noticed from the thermograms that a broad endothermic peak is observed in polymeric films at *ca.* 60–70°C and it is 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 65°C to 61°C after the polymer-salt complexation, and it is due to the increase in degree of amorphicity in SPE OCC. Figure 7 shows the temperature dependant conductivity variations for hot-pressed SPEs (1-*x*) PEO:*x* KI. $\lg \sigma$ - $1/T$ plots exhibit straight line behavior with an upward change in slope at *ca.* 70°C which is due to the well-known semi-crystalline to amorphous phase transition. The activation energy (E_a) values computed from the linear portion of all the plots (below *ca.* 70°C) by using the following Arrhenius equation:

$$\sigma(T) = \sigma_0 \exp(-E_a/kT) \text{ (S/cm)} \quad (1)$$

where σ_0 is the pre-exponential factor, E_a is the activation energy in eV, k is the Boltzmann constant and T is the temperature. The compositional dependent conductivity of SPEs (1-*x*) PEO:*x* KI is shown in Fig. 8. The low E_a in SPE OCC is due to high amorphous nature of the polymer that facilitates the fast motion in the polymer network and it is indicative of relatively easier ion migration in the newly synthesized system and hence it can be potentially used for electrochemical device applications.

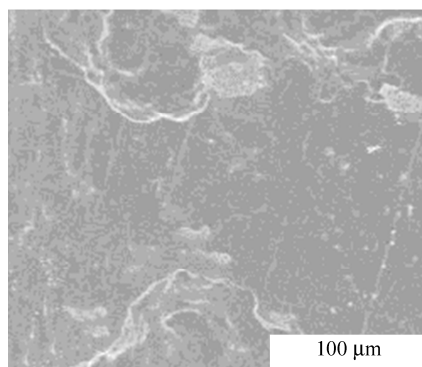


Fig. 5 SEM images of hot-pressed SPE OCC film (80PEO:20 KI)

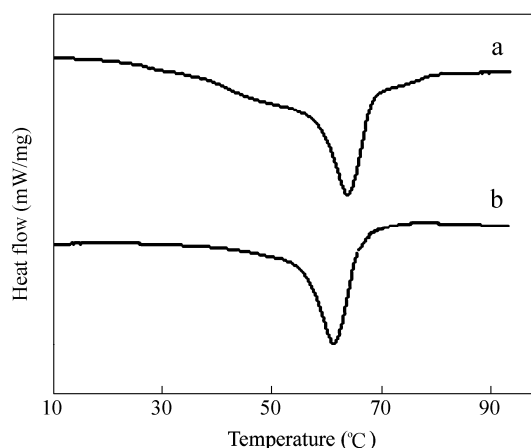


Fig. 6 DSC thermograms of (a) pure PEO and (b) hot-pressed SPE OCC film (80 PEO:20 KI)

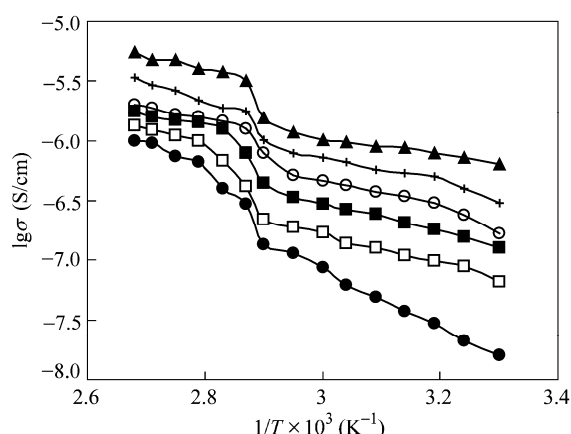


Fig. 7 Temperature dependent conductivity plots for hot-pressed SPE films (1-*x*) PEO:*x*KI
x = 5 (●), 10 (■), 20 (▲), 30 (+), 40 (o) and 50 (□) in wt%

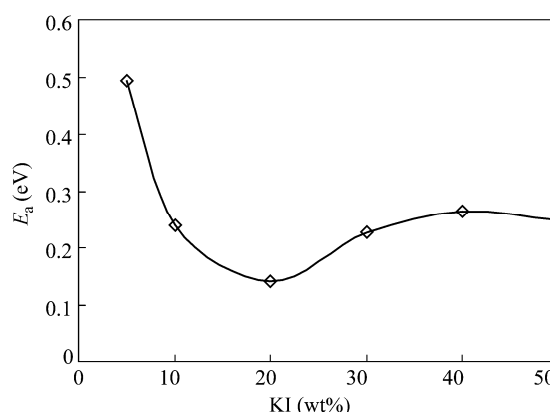


Fig. 8 Compositional dependent activation energy plot for hot-pressed SPE films (1-*x*) PEO:*x* KI

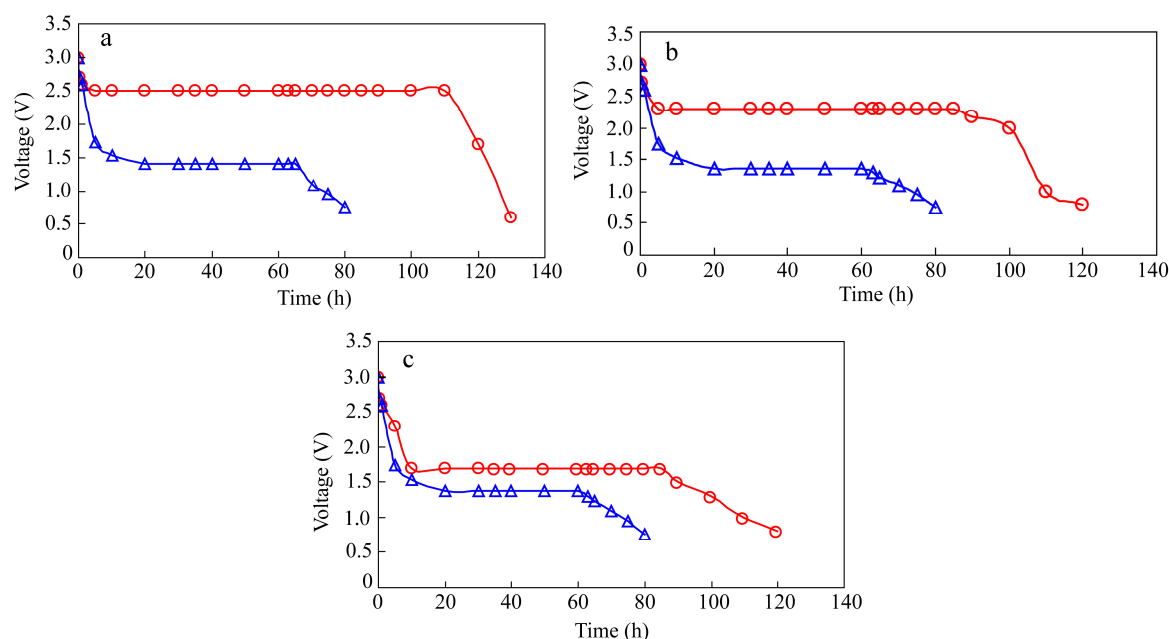


Fig. 9 Cell potential discharge profiles for the solid state polymeric batteries under 100 k Ω ($\circ$) and 50 k Ω (Δ) load resistances at different temperatures: (a) 40°C, (b) 27°C and (c) 15°C

Solid State Polymeric Battery Application

Figure 9 shows the electrochemical cell potential discharge profiles for a solid state polymeric cell under different loads *viz.* 100 k Ω and 50 k Ω at different temperatures (*viz.* 15°C, 27°C and 40°C). The open circuit voltage (OCV) of *ca.* 3 V is obtained for the both 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 potassium salt at the electrode/electrolyte interface^[30]. It can be clearly noticed that except for the initial potential drop, the OCV value of the batteries remained practically stable for *ca.* 80 and *ca.* 43 h during discharging through 100 and 50 k Ω respectively (*i.e.* during a low current drain state). However, the cell potential decreased relatively faster for discharge through 50 k Ω load (*i.e.* during higher current drain states). Table 2 lists some important cell parameters for polymeric cell, calculated in the plateau regions of the discharge profiles. On the basis of these studies, it can be observed that the newly investigated hot-pressed SPE OCC performed relatively superior at higher temperature and during low current drains.

Table 2. Some important cell parameters obtained from the plateau region of the discharge curves at different temperatures

Temperature (°C)	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 ($\text{mWh}\cdot\text{kg}^{-1}$)
40	100	2.5	2.00	250	38.81	3881.9
	50	1.4	1.12	56.0	12.17	486.95
27	100	2.3	1.84	184	32.06	2564.8
	50	1.37	1.09	58.91	11.37	489.13
15	100	1.7	1.36	136	17.95	718.01
	50	1.37	1.09	58.91	11.37	489.13

CONCLUSIONS

A new hot-pressed solid polymer electrolyte (SPE) membrane (80 PEO:20 KI) (wt%) has been investigated using a hot-press technique. The polymer-salt complexation and materials characterization have been confirmed by XRD, FTIR, SEM and DSC studies. Some basic ionic parameters, *viz.* σ , μ , n and E_{a} , measurements have

been done. The conductivity enhancement in SPE OCC is due to increase in number of mobile ions. The cell potential discharge characteristics of solid state polymeric battery have been studied under varying load conditions and at different temperatures, and the cell performed quite satisfactorily specially under low current drain states.

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