

# Effect of mixed cations in synergizing the performance characteristics of PVA-based polymer electrolytes for novel category Zn/AgO polymer batteries—a preliminary study

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**Abstract** Thin films of polymer electrolytes comprising of PVA and KOH (**A**) with and without the addition of zinc salts, viz., zinc acetate (**B**) and zinc triflate (**C**) as mixed cations were prepared via. solution casting method. The thermal stability and ionic conductivity of PVA–KOH solid polymer electrolyte (**A**) were improved by the partial substitution of KOH with zinc salts. Among the two salts, zinc triflate was found to improve both the physical as well as electrochemical properties of the PVA–KOH films more significantly than zinc acetate. An attempt to optimize the ratio of various components of polymer electrolytes, viz., polymer: KOH: zinc salt was also made, based on the dimensional stability and ionic conductivity values. Finally, the select category polymer film containing PVA–KOH–zinc triflate (**C**) in an optimum ratio of 40:35:25 was deployed in coin cell fabrication and subjected to charge–discharge studies with a view to demonstrate the possible electrochemical reversibility characteristics. Based on the encouraging results obtained from the cycling study, **C** type films [PVA–KOH–zinc triflate] qualify themselves as potential polymer electrolytes for use in rechargeable Zn/AgO polymer batteries.

**Keywords** Zn/AgO polymer battery · PVA polymer electrolyte · Mixed cation · Electrochemical reversibility

## Introduction

The inherent advantages of Zn-based energy systems that include low toxicity, low cost, high stability and the abundant availability of zinc resources have created an everlasting significance to rechargeable Zn batteries. However, certain hampering issues related to Zn electrode, such as redistribution/solubility of the Zn and the unacceptable capacity fade with progressive cycling behavior remains unsolved till date because of the aqueous KOH electrolyte being used in such batteries. But then, the well-known disadvantages of aqueous KOH electrolyte could be surpassed by the deployment of an all solid state Zn-polymer batteries. In other words, an all solid Zn-polymer battery gains importance [1–2], as the deployment of polymer electrolytes exclude problems associated with the leakage of liquid electrolyte, development of vapor pressure, and loss of electrode–electrolyte contact, thus qualify the same as potential electrolytes.

Having intrigued by the excellent performance of PVA-based polymer electrolytes in rechargeable alkaline battery applications, similar kind of an all solid Zn/AgO system with a PVA polymer matrix of apparent chemical stability and ionic conductivity [3] has been aimed through the present study. Since PVA-based polymer electrolytes are known for their higher ease to form films and hydrophilicity to interact with –OH groups, exploitation of the same has been attempted for the development of novel category Zn/AgO polymer batteries. Herein, the PVA polymer matrix swollen with water and alkali electrolyte solution with mixed cations would enhance the plasmification of alkaline PVA polymer electrolyte via  $\text{OH}^-$  transport across the electrolyte and the subsequent trapping of the same in the matrix [4]. It is noteworthy that PVA-based polymer electrolytes are of particular interest, since the PEO–PVA–

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KOH [5] composite polymer electrolytes deployed in alkaline Zn–Air and rechargeable Ni–MH battery applications [6] and the deployment of PVA/PECH and PVA/TEAC combination of membranes for fuel cells with grafting of quaternary amines [7, 8] are reported to exhibit encouraging results.

Similarly, among the various combinations of alkaline Zn batteries, the Zn/AgO batteries are bestowed with advantages such as high specific energy coupled with high specific power for high rate, weight, or size sensitive applications [9] despite the costly Ag electrodes. On the other hand, combination of zinc anode and silver oxide cathode along with polymer electrolytes is not reported so far, despite the fact that silver oxide cathode can be considered as one of the most versatile electrode materials. Therefore, a new kind of Zn/AgO battery with a solid polymer electrolyte, otherwise known as the Zn/AgO polymer battery explored for the first time through the current study assumes importance in terms of suppressed dendrite growth and enhanced safety with anticipated enhancement in energy density. Because literature reports on solid polymer electrolytes such as (PEO)–ZnBr<sub>2</sub> [10], PEO–KOH mixture [11], polyvinyl alcohol (PVA)–proton iodide systems [12] are available in combination with zinc anode and cathodes such as V<sub>6</sub>O<sub>13</sub> [13], MnO<sub>2</sub> [10], *N,N'*-dichlorohydantion [14] and dichloroisocyanuric acid [15] only.

Hence, the present study has a main focus on the development of novel category Zn/AgO polymer batteries containing suitably modified polymer electrolytes of PVA with mixed cations, with further interest on the possible exploitation of PVA chemistry in meeting out the requirements of polymer electrolytes consisting of PVA–KOH–Zn salt for energy storage applications. In addition, the highlight of the study is that the deployment of chosen category PVA-based polymer electrolytes could be extended in various other AgO cathode-based battery configurations also.

It is well known that despite the high ionic conductivity of PVA, which is driven through water vehicle and tunneling mechanisms [6], evaporation of KOH decreases the conductivity values, especially upon repeated cycling, due to the crystallization of polymer chain. Therefore, partial substitution of KOH with the addition of suitable inorganic salts was considered, in order to realize the mixed cation effects [4]. In this regard, salts such as zinc acetate and zinc triflate were chosen for the present study, based on the excellent performance characteristics exhibited by the acetate and triflate counterparts of lithium salts [16].

Thus, it has been ultimately decided to explore a combination of PVA with two kinds of zinc salts, viz. zinc acetate and zinc triflate individually in association with KOH, in order to realize synergistic effects due to polymer

electrolyte (PVA) and the mixed cations (KOH–zinc salt). A detailed investigation on the physical as well as electrochemical properties of polymer electrolytes based on PVA–KOH [A type], PVA–KOH–Zn acetate [B type] and PVA–KOH–Zn Triflate [C type] was made with a view to understand the effect of added zinc salt individually.

## Experimental

### Fabrication and optimization of polymer electrolytes

Polyvinyl alcohol (PVA), zinc acetate, and zinc trifluoro methane sulphonate (zinc triflate), purchased from Sigma Aldrich were used to fabricate polymer films of the present study.

Initially, a weighed quantity of PVA dissolved in warm distilled water was stirred continuously to get a homogenous solution. To the solution was added a given concentration of KOH and zinc acetate/zinc triflate, and the process of stirring was continued till the homogeneous solution turned to be slightly viscous. When an apparent viscosity was developed, the solution was poured onto a glass plate and evaporated at room temperature. The thickness of the polymer films was controlled by an in-house fabricated Doctor's blade apparatus to result in the formation of polymer films with a uniform thickness of 0.01 cm. Three types of polymer films (**A**, **B**, and **C**) with at least three ratios (1, 2, and 3) were developed by varying the quantities of KOH and zinc salts with an apparent mass of PVA (Table 1) and subjected to optimization studies subsequently. Such an optimization was done based on the ionic conductivity, dimensional/mechanical stability of the individual polymer membranes. The three types of solid polymer electrolytes prepared were PVA–KOH, (**A** type) and PVA–KOH–zinc acetate (**B** type), and PVA–KOH–zinc triflate (**C** type), and the details of the ratios (1–3) of individual components chosen for the study are furnished in Table 1.

Furthermore, crystal structure and thermal stability of the polymer electrolyte films were characterized by X-ray diffraction (XRD) and TGA studies. Finally, electrochemical characterization (impedance, CV, and charge–discharge) of such polymer electrolytes was done using SS/polymer/SS, (SS) Zn/polymer/Zn (SS), and (SS) Zn/polymer/AgO (SS), (where SS is stainless steel) type of electrochemical cells assembled.

### Electrode preparation

The anode was prepared by pelletizing the powered mixture of dried PVA (2 wt%), KOH (5 wt%) and ZnO (93 wt%) in distilled water. Similarly, the cathode was prepared by

**Table 1** Dimensional stability and composition of solid polymer electrolytes

Type of polymer electrolyte	Composition of the solid polymer electrolyte				Dimensional Stability
	PVA	KOH	Zinc acetate	Zinc triflate	
A1	60	40	–	–	Fairly stable
A2	55	45			Fragile
A3	40	60			Fragile
B1	40	25	35	–	Fairly stable
B2	40	30	30		Fairly stable
B3	40	35	25		Fairly stable
C1	40	25	–	35	Stable
C2	40	30		30	Stable
C3	40	35		25	Stable

pelletizing a similar composition of powders of dried PVA and KOH with 93 wt % Ag. The as prepared electrodes were pelletized over silver mesh and punched out for 20 mm diameter (1 mm thickness), for deployment in 2,016 stainless steel coin cells. Herein, a weighed amount of 2.0 g of anode powder and about 1.75 g of cathode powder were used to prepare electrodes.

#### Instrumentation

Thermogravimetric analysis (TG) of the membranes was performed with TA instruments, Model SDTQ600. The measurement was carried out from room temperature to 250 °C with a heating rate of 25 °C/min. The crystal structure of the polymer film was examined by PANalytical, (X'per PRO model) X-ray diffractometer with CuK $\alpha$  radiation (2.2 kW Max) for 2 $\theta$  angles between 0° to 70°. The ionic conductivity of the films was determined by the AC impedance method, using an IM6 BAS electrochemical analyzer. The frequency range used was 10 mHz to 100 kHz, and the amplitude was 5 mV. Cyclic voltammetry was carried out for cells containing SS/polymer/SS, (SS) Zn /polymer/Zn (SS), and (SS) Zn/polymer/AgO (SS), using linear potential sweep voltammetry, at a scan rate of 50 mV/s, throughout the study. The polished stainless steel disc was used as the

working electrode and a Zn/Ag disc (20 mm diameter) served as both the counter electrode and reference electrode.

## Results and discussion

### Optimization of PVA:KOH ratio

The dimensional stabilities of various solid polymer electrolyte films fabricated with PVA-KOH (A), PVA-KOH-Zn acetate (B), and PVA-KOH-Zn triflate (C) are given in Table 1. It is obvious from Table 1 that the addition of Zn salt is highly essential to impart dimensional stability. Because dimensional stability problem is found to be more severe for type A than type B films. On the other hand, type C films exhibit good dimensional stability that may be attributed to the effect of Zn triflate salt. So, it is understood that PVA, being hydrophilic in nature with the addition of KOH alone has resulted in extremely fragile nature of polymer films (A), thereby indicating the requirement of salt addition that may offer filler effect to the polymer films. Therefore, two types of zinc salts viz., one with readily hydrolyzable counterpart (CH<sub>3</sub>COO<sup>-</sup>) and the other with fairly hydrolyzable counterpart (CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) were chosen for the study to understand the effect of each salt individually.

**Table 2** Impedance and conductivity data of the solid polymer electrolytes

Type of polymer membrane	Thickness of the membrane (cm)	Composition of the alkaline solid polymer (PVA/KOH/Zn salt)				Impedance $R_b$ ( $\Omega$ )	Conductivity $\sigma$ (S cm <sup>-1</sup> )
		PVA	KOH	Zinc acetate	Zinc triflate		
A1	0.01	60	40	–	–	0.71	$7.92 \times 10^{-3}$
A2	0.01	55	45			2.25	$1.51 \times 10^{-3}$
A3	0.01	40	60			4.07	$1.38 \times 10^{-3}$
B1	0.01	40	25	35	–	0.63	$5.37 \times 10^{-3}$
B2	0.01	40	30	30		0.58	$9.76 \times 10^{-3}$
B3	0.02	40	35	25		0.93	$1.57 \times 10^{-2}$
C1	0.01	40	25	–	35	1.00	$5.70 \times 10^{-3}$
C2	0.02	40	30		30	1.30	$8.71 \times 10^{-3}$
C3	0.01	40	35		25	0.40	$2.54 \times 10^{-2}$

Herein, the role of various components such as PVA, KOH, water content, and the added zinc salt in imparting dimensional stability to the polymer electrolytes may be understood as follows: Based on the reports of Sang et al. [17], it is understood that if the water content in the electrolyte membrane is less, the excessive KOH will get precipitated to make the polymer matrix stiff. However, fragile polymer electrolytes (A type) are obtained in the present study, thus eliminating the possibility of lesser water content as the reason for the poor dimensional stability. Rather, the fragility of such films may be correlated to the higher water and/or KOH content, as derived from the dimensional stability observations of A1–A3 polymer electrolytes [Table 1]. Because it is noteworthy that PVA, well known for its high water-absorbing and water-holding capability may also impart and enhance the water content when the amount of the same is increased. Based on this reason only, the amount of PVA has been fixed as 40%, which is noteworthy.

Furthermore, the enhanced conductivity values observed for both the B and C category electrolyte membranes with respect to those of A1–A3 films (Table 2) substantiate the fact that the reduced water content has neither affected the conductivity of the polymer films nor their dimensional stability.

While considering the effect of added zinc salt, the acetate salt has little effect in enhancing the dimensional stability of polymer films (B1–B3), due to the factor of hydration. On the other hand, triflate salt with a bulky group has enhanced the dimensional stability of PVA–KOH–zinc triflate (C1–C3) films via filler effect. Hence, it is basically understood that the fabrication of dimensionally stable polymer films require a minimum composition of 40% PVA matrix along with more or less equal ratios of KOH and Zn triflate salt. Herein, the composition of PVA (for B and C type films) has been optimized as 40%, based on various factors such as homogeneity, viscosity, dimensional stability, AC impedance, and conductivity measurement values of the polymer films, in addition to the water content factor of PVA, as discussed already.

It is quite interesting to note that even though homogeneity was observed for all the three chosen ratios of A, B and C type of films, the polymer films with higher polymer content (60%) without any Zn salt (A type) and the films with lower polymer content (40%) with the added zinc salts (B and C types) were found to produce better results in all the aforesaid characterizations (Tables 1 and 2). Since higher PVA content (60%) is not preferred in view of better dimensional stability, B and C type films are only preferred ultimately. Hence, it is understood that the performance characteristics of PVA-based polymer electrolytes depend upon the type of added zinc salt, which is responsible for the mixed cation effect.

Conductivity and composition of the solid polymer electrolytes (SPE)

Impedance spectrum of SS/SPE/SS cell with optimized PVA–KOH and PVA–KOH–zinc salts compositions were measured, and further specific conductance ( $\sigma$ ) of the SPE was calculated from the Bode plot using the equation,  $\sigma = l/AR_b$ , where “ $l$ ” is thickness of the SPE and “ $A$ ” is the area of the SS electrode. The ionic conductivity of SPE, with varying concentrations of PVA, KOH, and zinc salts was studied, and the results are included in Table 2.

Among the A type of polymer electrolytes, the mass ratio of PVA/KOH as 60:40 in A1 was found to exhibit a maximum ionic conductivity of  $7.9 \times 10^{-3} \text{ Scm}^{-1}$  at 27 °C (than A2 and A3) along with mechanical stability that may render easy handling of the films during cell construction and further characterization studies. Similarly among the B and C type of polymer films, it was interesting to note that at low concentrations of zinc salts,  $\sigma$  was about  $1.57 \times 10^{-2}$  (zinc acetate) and  $2.548 \times 10^{-2}$  (zinc triflate) that has decreased with an increase in the concentration of zinc salt, probably due to ion pair formation [18]. Hence, it is concluded that the optimum amount of PVA and Zn salt are 40% and 25%, respectively, thus substantiating the results derived from the dimensional stability view point. However, based on the appreciable ionic conductivity values (Table 2), three polymer films, viz., A1, B3, and C3 were chosen for further physical characterization such as TGA and XRD.

Since the viscosity of polymer electrolytes depends upon the weight ratio of polymer, KOH, and added zinc salt [19], the present study favors the addition of an optimum amount of 25% of zinc salt, irrespective of the type of films (B or C) being fabricated. On the contrary, higher concentration of zinc salts (30% and 35%) have exhibited lesser conductivity values ( $10^{-3}$ ) and more specifically, if the salt concentration is higher than that of KOH (B1, B2, C1, and C2), the conductivity values are found to decrease accordingly. Hence, it is understood that the effect of added salt has a vital and crucial role in enhancing the conductivity, as evidenced in Table 2. Furthermore, it is obvious that the addition of optimized quantity (25%) of zinc salt has favorable effects (B3 and C3) rather than higher salt concentration, as indicated by the ionic conductivity values. Therefore, the preliminary qualitative and quantitative characterization results of polymer electrolytes strongly emphasize the optimum component ratio as 40:35:25 (PVA/KOH/zinc salt) for any zinc salt combination. In other words, it is evident from Table 2 that the combination of PVA–KOH–zinc salt in 40:35:25 ratio (B3 and C3) are found to exhibit higher ionic conductivity values ( $10^{-2}$  range), thus recommending the ratio 40:35:25 as an ideal composition to prepare PVA-based polymer films with

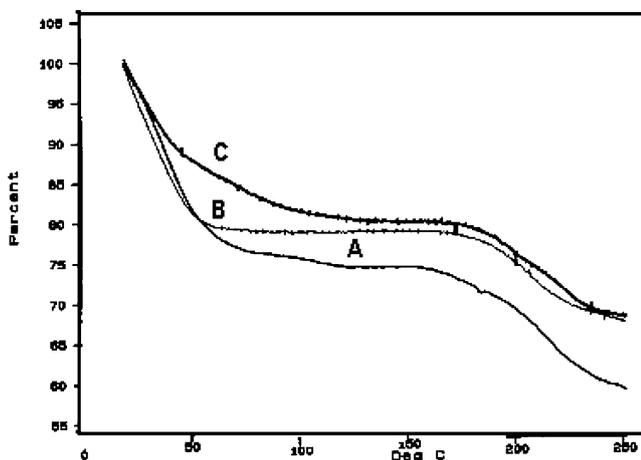
mixed cations. More particularly, C3 film has exhibited the highest conductivity ( $2.54 \times 10^{-2} \text{ S cm}^{-1}$ ) and lowest impedance ( $0.40 \Omega$ ), thereby, optimizing the components as PVA–KOH–zinc triflate and the composition ratio as 45:35:25. So, it is concluded that the deployment of PVA-based polymer electrolytes for device applications would definitely require an optimum amount of 25% zinc triflate salt addition.

#### Thermogravimetric analysis of solid polymer electrolytes

The thermogravimetric curves of A1, B3, and C3 polymer films are shown in Fig. 1. The weight loss in A1 type polymer film (without any zinc salt) was found to be very high (35%), when compared with B3 and C3 type of polymer films with added acetate and triflate zinc salts, respectively (20%, 15%). Hence, it is implied that the addition of mixed cation in the form of zinc salts is highly essential to improve the thermal stability of PVA-based polymer electrolyte films. Furthermore, Lewandowski et al., have reported that the PVA–KOH films are not stable at temperatures above 150–160 °C [11], as they undergo decomposition to form brown films. On the contrary, polymer film with PVA–KOH–zinc triflate in 40:35:25 ratio (C3) presented minimum weight loss (15%) only, thus accounting for high thermal stability. So, it is understood from TGA studies also that the optimized composition is C3 rather than B3 and A1, despite the comparable conductivity values exhibited by all the three films.

#### XRD analysis of solid polymer electrolytes

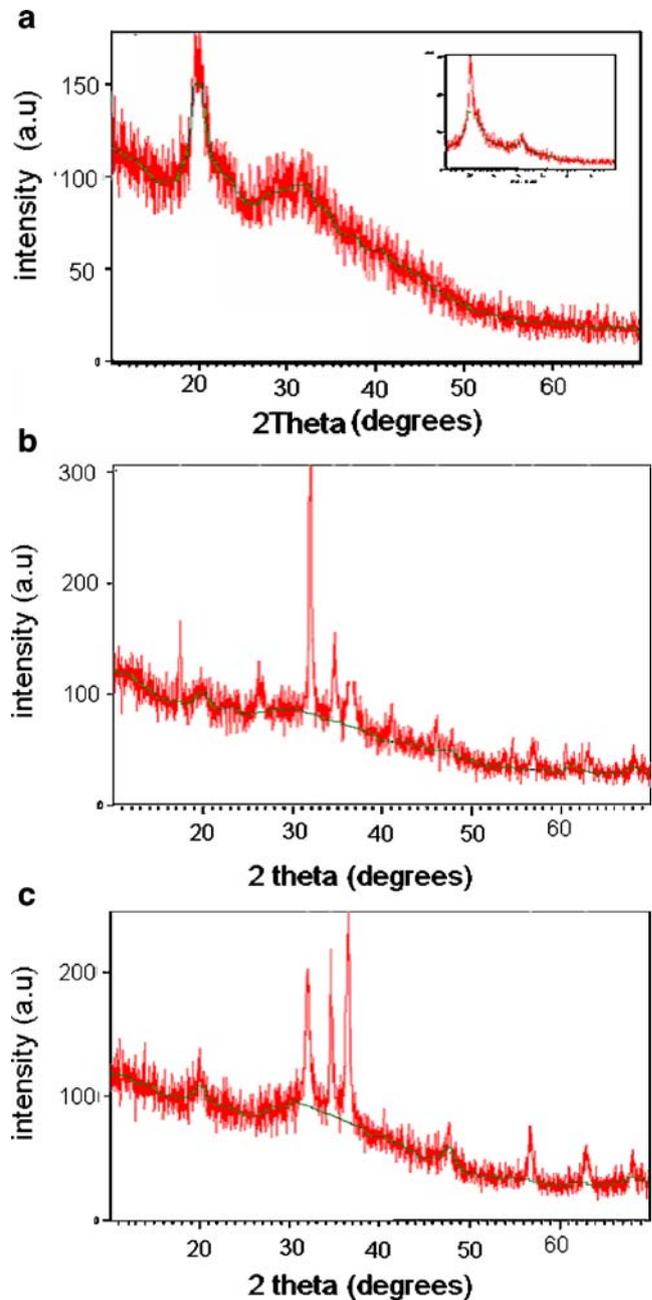
Basically, the ionic conductivity of the polymer electrolyte is due to the transport of cation and anion charge carriers in a polymer matrix. The ionic mobility is increased by



**Fig. 1** Thermogravimetric (TG) behavior of PVA-based polymer electrolytes

segmental motion of the PVA polymer host, and the ionic conductivity is mainly localized to the amorphous phase [20].

The results of XRD analysis of A1, B3, and C3 polymer membranes are shown, respectively, in Fig. 2a, b, and c. The intensity of the peak observed at  $2\theta=20^\circ$ , attributed normally to the pure PVA (insert in Fig. 2a) was reduced due to the addition of KOH (Fig. 2b). Furthermore, it is quite interesting to note that the intensity of the PVA peak



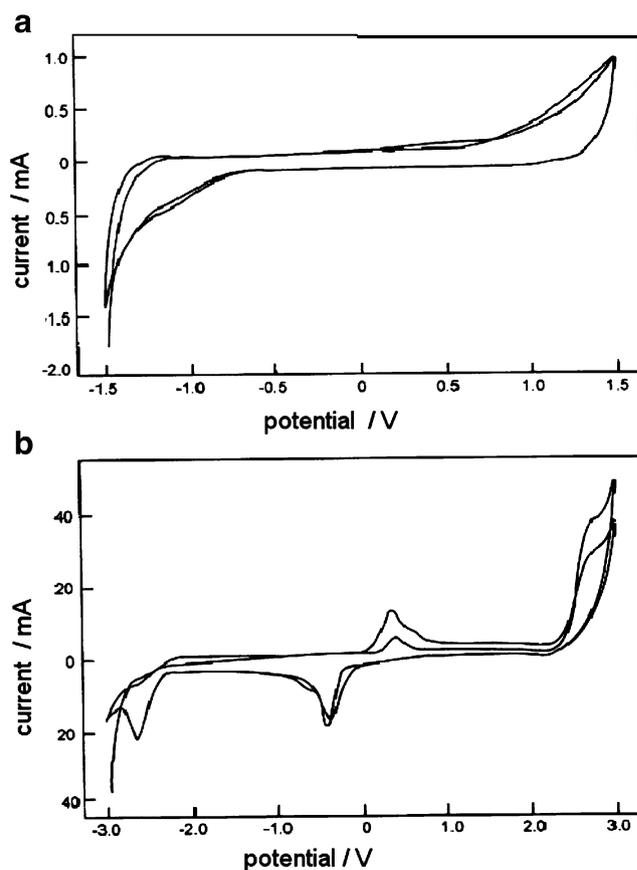
**Fig. 2** XRD pattern recorded for **a** A1 polymer electrolyte; *Inset a* XRD pattern of pure PVA powder. **b** B3 polymer electrolyte. **c** C3 polymer electrolyte

was found to get reduced largely, when zinc salts (acetate and triflate) were added to PVA–KOH polymer membrane (B3 and C3). Since the decrease in peak intensity of PVA is associated with the increasing order of amorphous domain, it is expected that the effect of mixed cations due to the added zinc salts in KOH has significantly reduced the crystallinity of PVA through plasification, thus rendering the possibility to realize higher ionic conductivity values. Such a correlation relating the reduced crystallinity of PVA via plasification and the enhanced ionic conductivity values of polymer films due to the addition of zinc salts in KOH holds good for the present set of polymer electrolyte films, thus emphasizing the significant role played by the mixed cations in improving the physical as well as electrochemical properties.

Based on the observations of dimensional stability, conductivity, thermogravimetry, and XRD studies, it is obvious that the added zinc salts (acetate and triflate) have significant effect over the performance characteristic of PVA–KOH (A) polymer electrolyte. In particular, TGA, XRD, and ionic conductivity studies clearly demonstrate the superior effect of zinc triflate salt addition compared to that of zinc acetate. So, further studies related to the characterization of PVA-based polymer electrolytes were restricted with respect to PVA–KOH–zinc triflate (C3) electrolytes only.

#### Reversibility of $\text{Zn}/\text{Zn}^{2+}$ and $\text{Ag}/\text{Ag}^{2+}$

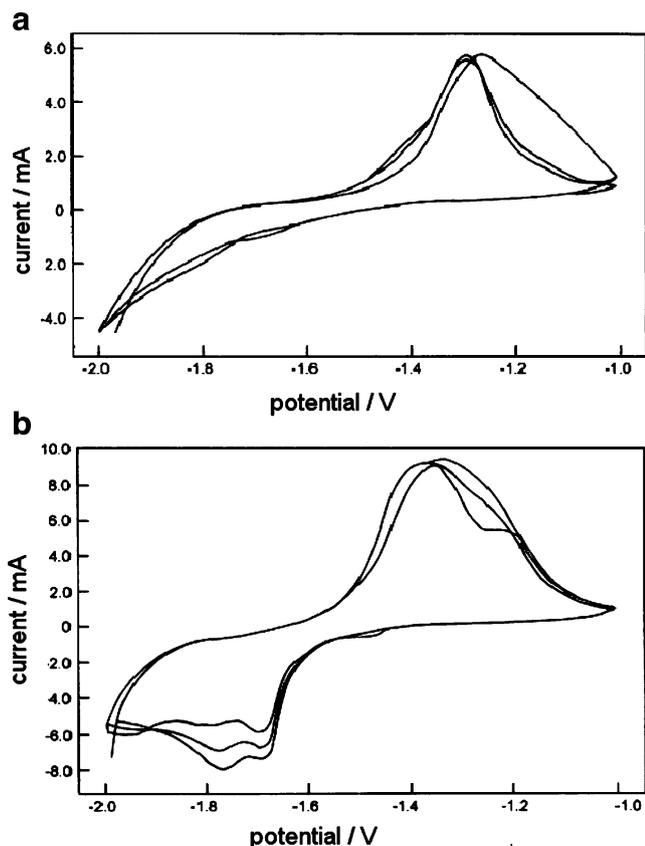
Cyclic voltammograms of the cells with configuration SS/PVA–KOH/SS [A1] and SS/PVA–KOH–zinc triflate/SS [C3] are shown in Fig. 3a and b, respectively. Highly reversible Zn plating/stripping at the metal/membrane interface was observed for the membrane with zinc triflate (C), whereas essentially no current was observed for the membrane without salt (A). The electrochemical stability window of the polymer electrolyte without salt was found to be  $-1$  to  $+1$  V, whereas for ‘C’ type polymer membrane with salt, it was around  $-2.2$  to  $+2.2$  V. It is already reported [21] that the added zinc salt in polymer electrolytes would cause a change in the electrochemical window. In other words, Xu et al. [21] have reported a significant decrease in the electrochemical stability window, from 5.0 to 2.8 V, due to the addition of zinc salt. On the contrary, the polymer electrolyte of the present study has encountered a reasonable increase in the electrochemical stability window, from 1.0 to 2.2 V via the addition of Zn triflate, which is quite interesting. Therefore, it is believed that such an increase in the  $\text{H}_2$  and  $\text{O}_2$  overpotential ( $\approx 1.2$  V) observed in the present case is due to the change in the electrochemical stability window driven by the added zinc salt. Herein, the higher electrochemical stability window of



**Fig. 3** Electrochemical stability window of **a** A1 polymer electrolyte. **b** C3 polymer electrolyte

‘C’ type polymer membranes with zinc triflate salt would enable higher electrical rechargeability of the secondary cells. This finding is also in accordance with the optimization results derived from other characterization studies.

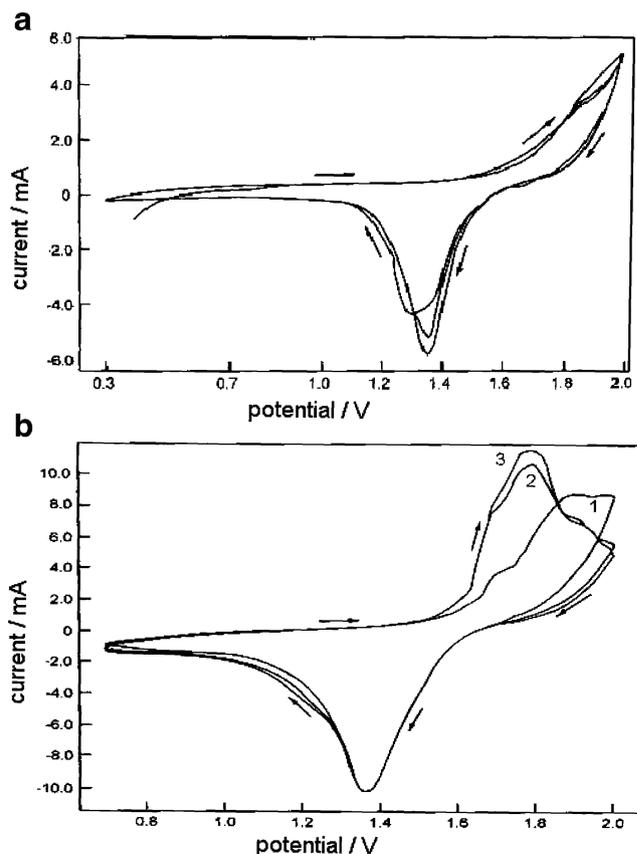
Cyclic voltammograms of cells with configuration such as SS/Zn/PVA–KOH (A1)/AgO/SS and SS/Zn/PVA–KOH–zinc triflate (C3)/AgO/SS are shown in Fig. 4a, b (to demonstrate the  $\text{Zn}/\text{Zn}^{2+}$  reversibility) and in Fig. 5a and b (to demonstrate the  $\text{Ag}^+/\text{Ag}$  reversibility). Here, the Zn plating/stripping currents of polymer membrane in the  $-2$  to  $-1$  V potential region without salt (A) exhibit large anodic and reduced cathodic activity (Fig. 4a), whereas the anodic and cathodic activities of polymer membrane with zinc triflate (type C) are highly reversible (Fig. 4b). The results of ‘A’ type (PVA–KOH) polymer membrane suggest that the total quantity of zinc oxidized during anodic activity was not available during cathodic activity, possibly due to the diffusion of zincate ions (discharge product) away from the electrode vicinity [22]. In other words, the presence of large excess of KOH (40%) without any added salt accelerates the dissolution mechanism of zinc anode, as in the case of aqueous electrolyte that results in large anodic



**Fig. 4** Demonstration of  $\text{Zn}/\text{Zn}^{2+}$  reversibility using **a** A1 polymer electrolyte. **b** C3 polymer electrolyte

activity, which is evidenced by the peak at (-1.3 V). This phenomena was not observed in the ‘C’ type polymer membranes (with zinc triflate), probably due to the formation of KOH–zinc triflate complex in the polymer membrane with salt. Similarly, the AgO/plating and stripping currents of the polymer membrane in the potential region 0.8 to 2.0 V with salt was also more reversible than in the polymer membrane without zinc salt [type ‘A’] (Fig. 5a and b). In addition, the Faradaic yields on the voltammograms are calculated to be 43 Coulombs for PVA–KOH electrolyte membrane (A-type) [Fig. 5a] and 217 Coulombs for PVA–KOH–zinc triflate electrolyte membrane (C-type) [Fig. 5b], thus favoring the significant effect of added zinc salt. Herein, it is noteworthy that the appearance of very first anodic peak was assigned [3] to the formation of  $\text{Ag}_2\text{O}$ , i.e., the small peak at 1.7 V in Fig. 5b was corroborated to the formation of  $\text{Ag}_2\text{O}$ . So, the subsequent and prominent peak at 1.8 V was believed be due to the formation of AgO, which was only taken in to consideration for discussion in the present study.

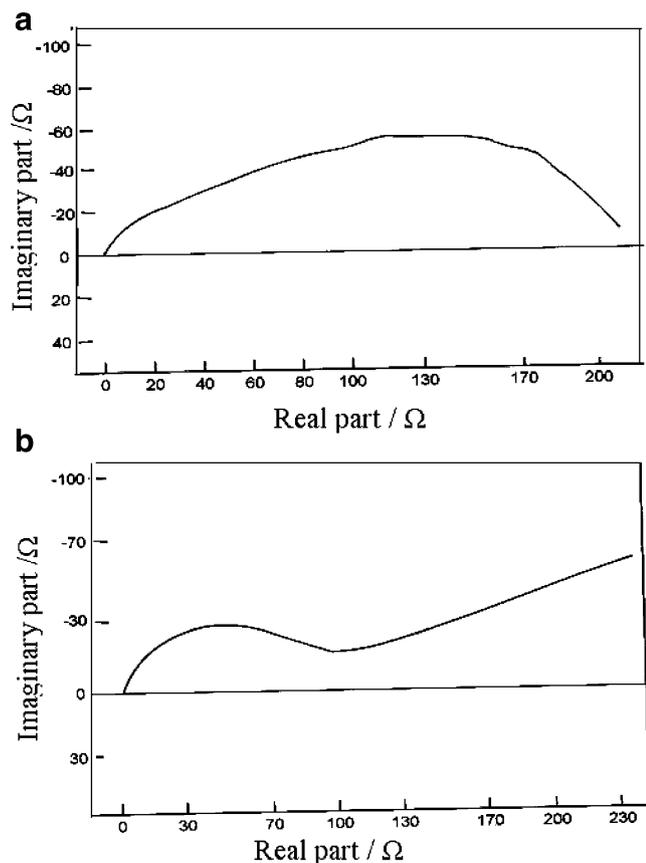
Hence, the results clearly demonstrate the diffusion of  $\text{Zn}^{2+}$  and  $\text{Ag}^{2+}$  ions in the polymer membranes and that the  $\text{Zn}^{2+}$  and  $\text{Ag}^{2+}$  ions are capable of dissolution into and deposition from these membranes. The low overpotential



**Fig. 5** Demonstration of  $\text{Ag}/\text{Ag}^{+}$  using **a** A1 polymer electrolyte. **b** C3 polymer electrolyte

corresponding to the plating/stripping of  $\text{Zn}/\text{Zn}^{2+}$  and  $\text{Ag}/\text{Ag}^{2+}$  in the polymer membranes indicates a possible lower metal/polymer interfacial resistance, including the kinetic resistance associated with Zn/Ag electron transfer reaction [18].

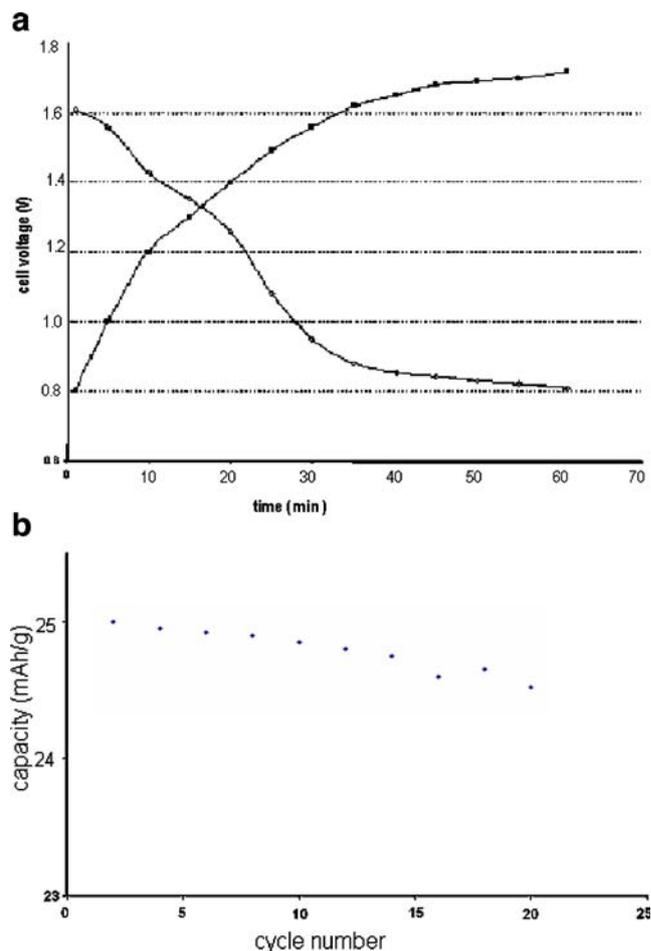
The interfacial stability of zinc in the A1 and C3 type polymer membranes was also examined using impedance analysis. The a.c. impedance spectra (Fig. 6) consisted a single constant phase element at high frequencies, representing the charge-transfer resistance and a linear part at the low frequency, corresponding to the adsorption of -OH species on the zinc surface [23]. A comparative study of the impedance spectra of polymer membrane with and without zinc triflate type A and C (Fig. 6a and b) reveal that the charge-transfer resistance of zinc ions in the polymer membrane had improved, when zinc triflate was added to it (lower resistance value of the type C polymer membrane). Thus, it is reflected from impedance measurement studies also that the addition of zinc salts is mandatory, with a special reference to the addition of optimized amount of zinc triflate salt in order to realize better electrochemical activity, as far as the pure PVA–KOH-based polymer electrolyte (A) membranes are concerned.



**Fig. 6** Impedance behavior of **a** Al polymer electrolyte. **b** C3 polymer electrolyte

#### Zn/ solid polymer electrolyte /AgO cell

The C type solid polymer electrolyte consisting of PVA–KOH–zinc triflate possess good anodic and cathodic stability, high ionic conductivity, and good reversibility of Zn/Zn<sup>2+</sup> and Ag/Ag<sup>2+</sup> couples at the interface. Hence, it is obvious that this electrolyte would be a good candidate for rechargeable zinc battery applications. Coin cells comprising of PVA–KOH–Zn triflate as the electrolyte (C), zinc oxide as anode, and silver as cathode have been assembled and subjected to charge–discharge studies. Typical galvanostatic charge–discharge curve pattern exhibited by C3 films in a full cell assembly of Zn/C3 film/AgO, at a current density of 200  $\mu\text{A}/\text{cm}^2$  is presented in Fig. 7a. The faradaic yield on Fig. 7a is not encouraging, may be due to the reason that the electrode has been made without any conducting additives like carbon, super P, acetylene black, etc. However, it is believed that the conductivity of the same could be improved by way of introducing suitable and an optimum amount of conducting material along with the added binder, viz. PTFE. To have more insights, a study on the optimization of amount or ratio of binder/conducting material has to be done exclusively with a view to realize an enhanced faradaic yield, which is reserved for our future



**Fig. 7 a** Typical charge–discharge characteristics of coin cells fabricated with C3 polymer electrolyte in the Zn/C3 polymer film/AgO cell assembly. **b** Capacity vs. cycle number behavior of C3 polymer electrolyte in the Zn/C3 polymer/AgO coin cell

study. But then, the observed capacity behavior of the Zn/AgO polymer cells of the present study is in accordance with the reported results of Zn/MnO<sub>2</sub> polymer cells [18], thus demonstrating the electrochemical reversibility of the newly suggested Zn/AgO polymer battery configuration. Similarly, when the cell containing Zn/C3 film/AgO was subjected to 20 cycles, a minimum specific capacity loss of about 3% (Fig. 7b) has been noticed, which is quite interesting. This result is in favor of the fact that the optimized C3 polymer films possess good electrochemical stability, desired for energy storage applications.

#### Conclusions

A new kind of Zn/AgO polymer battery containing suitably modified PVA-based polymer electrolyte with the addition of select category zinc salts (zinc acetate and zinc triflate) has been explored through the present study. The possibility of realizing synergistic effect due to the plified PVA

matrix and mixed cations (KOH + zinc salts) has been attempted in order to obtain improved electrochemical performance in the rechargeable Zn/AgO polymer system. In this regard, three types of polymer films (A, B, and C) were developed, and based on the performance characteristics of the said polymers, optimization of components of polymer electrolytes was carried out systematically. Based on the results of physical as well as electrochemical characterization studies, the optimum combination was found to be PVA–KOH–zinc triflate and the optimum ratio was 40:35:25 (C3 film). Such an optimized polymer electrolyte when deployed in Zn/AgO polymer cell assembly has exhibited excellent reversibility and electrochemical stability upon cycling, thus qualifying the same for energy storage applications.

## References

1. Gray FM Polymer electrolytes RSC materials monographs. The Royal Society of Chemistry, Cambridge
2. Tarascon JM, Armand M (2001) *Nature* 414:359
3. Lewandowski A, Skorupska K, Malinska J (2000) *Solid State Ion* 133:265
4. Mcbreen J, Yang XQ, Lee HS (1995) *J Electrochem Soc* 142:348
5. Yang CC (2002) *J Power Sources* 109:22
6. Yang CC, Lin SJ (2002) *Mater Lett* 57:873
7. Agel E, Bouet J, Fauvarque JF, Yassir H (2001) *Ann Chim Sci Mater* 26:59
8. Agel E, Bouet J, Fauvarque JF (2001) *J Power Sources* 101:267
9. Karpinski AP, Russel SJ, Serenyi JR, Murphy JP (2000) *J Power Sources* 91:77
10. Hagan WP, Latham RJ, Linford RG, Vickers SI (1994) *Solid State Ion* 70/71:666
11. Fauvarque JF, Guinot S, Bouziri N, Salmon E, Penneau JF (1995) *Electrochim Acta* 40:2449
12. Tedjar F (1994) *J Power Sources* 48:285
13. Singh K, Tiwari RU, Deshpande VK (1993) *J Power Sources* 46:65
14. Udhayam R (1993) *Port Electrochim Acta* 11:237
15. Gray FM (1991) *Solid polymer electrolytes: fundamentals and technological applications*. VCH Publications, New York
16. Gray FM Polymer electrolytes RSC materials monographs. The Royal Society of Chemistry, Cambridge
17. Sang S, Zhang J, Wu Q, Liao Y (2007) *Electrochimica Acta* 52:7315
18. Girish kumar G, Sampath S (2003) *Solid State Ion* 160:289
19. Muniyandi N, Kalaiselvi N, Periasamy P, Thirunakaran R, Ramesh babu B, Premkumar T, Gopukumar S, Raghavan M (2001) *J Power Sources* 96:14
20. Yang CC (2004) *Mater Lett* 58:33
21. Xu JJ, Ye H, Huang J (2005) *Electrochem Commun* 7:1309
22. Vatsalarani J, Trivedi DC, Geetha S, Warriar PC (2006) *J Power Sources* 158:1484
23. Hampson NA, McNeil AJS (1985) *J Power Sources* 15:61