

# Alkaline composite PEO–PVA–glass-fibre-mat polymer electrolyte for Zn–air battery

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## Abstract

An alkaline composite PEO–PVA–glass-fibre-mat polymer electrolyte with high ionic conductivity ( $10^{-2}$  S  $\text{cm}^{-1}$ ) at room temperature has been prepared and applied to solid-state primary Zn–air batteries. The electrolyte shows excellent mechanical strength. The electrochemical characteristics of the batteries were experimentally investigated by means of ac impedance spectroscopy and galvanostatic discharge. The results indicate that the PEO–PVA–glass-fibre-mat composite polymer electrolyte is a promising candidate for application in alkaline primary Zn–air batteries.

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*Keywords:* Composite polymer electrolyte; PEO–PVA blend; Ionic conductivity; Zinc–air battery

## 1. Introduction

Solid polymer electrolytes (SPEs) have been studied extensively in recent years for application in many electrochemical devices, such as cellular phones, thin credit cards, and laptop computers [1]. Polymer complexes consisting of polyethylene oxide (PEO), plasticizers, and alkali metal salts, discovered by Wright and co-workers [2,3] and Armand et al. [4], are solvent-free polymer electrolytes. Although a PEO-based SPE can form a dimensionally stable film, its conductivity at ambient temperature is in the range of  $10^{-7}$  to  $10^{-8}$  S  $\text{cm}^{-1}$ . This value is too low for application in electrochemical devices. In order to enhance the conductivity, several approaches have been suggested. Both polymer blends, i.e. polymers modified with a plasticizer or a mixture of solvents, and gel electrolytes have been explored. The main goal of these studies has been to obtain films with a high fraction of amorphous phase, which exhibits a much higher conductivity than the crystalline phase.

Several research studies have focused on PEO-based electrolytes with lithium salts and organic solvents. The polymer lithium system appears to be the most widely studied due to its potential application in batteries of high specific energy. Only a few alkaline solid polymer electrolytes based on the

PEO–KOH system have been investigated [5–8]. Lewandowski et al. [9] studied a polyvinyl alcohol PVA–KOH alkaline polymer electrolyte system by ac impedance and cyclic voltammetry methods. It was found that the ionic conductivity of the PVA–KOH–H<sub>2</sub>O (~40 wt.% PVA, 25–30 wt.% KOH, 30–35 wt.% H<sub>2</sub>O) polymer electrolyte was of the order of  $10^{-3}$  to  $10^{-4}$  S  $\text{cm}^{-1}$ , and  $E_a$  was 22–28 kJ/mole.

In this work, we report the preparation and properties of an alkaline composite polymer electrolyte based on a PEO–PVA–glass-fibre-mat system. In general, this composite electrolyte can be applied in all alkaline batteries systems. For example, the electrolyte has been used in the nickel–metal-hydride (Ni–MH) rechargeable battery system [10] and exhibits very good electrochemical performances at a low-to-medium rate cycling condition. A primary Zn–air cell has been selected to study the performance of the alkaline composite PEO–PVA–glass-fibre-mat polymer electrolyte. The Zn–air batteries [11–17] possess high specific energy, i.e. more than 200 Wh  $\text{kg}^{-1}$  compared with other Zn-based alkaline batteries. This is due to the unlimited and free supply of O<sub>2</sub> from the atmospheric air, which is not embodied within the cell. Also, Zn–air batteries offer many advantages, which include a much flatter working voltage, a higher capacity density which is independent of load and temperature, longer dry-storage time, and use of environmentally friendly and low-cost active materials. In this work, the solid-state Zn–air cell consists of an alkaline composite PEO–PVA polymer electrolyte combined with a

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zinc gel anode and an air diffusion cathode. The electrochemical performance of solid state Zn–air battery had also been examined by ac impedance spectroscopy and a galvanostatic discharge tests.

## 2. Experimental

PEO (Mw 100,000 Aldrich), PVA (Mw 80,000 Aldrich) and KOH (Merck) were used as-received without further treatment. The alkaline composite blend polymer electrolyte films were prepared by a solvent casting method. The appropriate weight ratios of PEO, PVA and KOH were dissolved individually in water. The viscous polymer solution was stirred continuously until the polymer mixture became a homogeneous viscous liquid. The resulting homogeneous polymer solution was poured into a petri dish with glass-fibre-mat and weighed immediately. The excess water was then allowed to evaporate slowly in a vacuum oven. After water evaporation, the Petri dish with the film was weighed again. The composition of blend polymer electrolyte was calculated from the mass balance. The thickness of the composite polymer films was controlled at between 0.30 and 0.60 mm. Conductivity measurements were made for the composite polymer electrolyte film by an ac two-terminal method. The composite polymer electrolyte samples were sandwiched between SS304 stainless-steel, ion-blocking electrodes, each of surface area  $0.785 \text{ cm}^2$ , in a spring-loaded glass holder. A thermocouple was located close to the polymer electrolyte film for temperature measurement. Cyclic voltammetry and ac impedance measurements were carried out using Autolab PGSTAT 30 equipment (Eco Chemie B.V., The Netherlands). The ac frequency range was 1 MHz to 0.01 Hz with an amplitude of 5 mV. The impedance of the composite polymer film was examined at 20–70 °C. Experimental temperatures were maintained within  $\pm 0.1 \text{ }^\circ\text{C}$  by a convection oven.

The carbon slurry for the gas-diffusion layer was prepared from a mixture of 70 wt.% Shawinigan acetylene black (AB50) with a specific surface area of  $80 \text{ m}^2 \text{ g}^{-1}$  and 30 wt.% PTFE (Teflon-30 suspension) as a wet-proofing agent and binder. The slurry was coated on a Ni-foam substrate (as a current collector), then pressed at  $100 \text{ kg cm}^{-2}$ . The gas-diffusion layer was then sintered at 300 °C for 30 min. The active layer of the air electrode was then prepared by spraying a mixture of 15 wt.% PTFE, 5–10 wt.%  $\text{KMnO}_4$ , 60 wt.% Vulcan XC-72R with a surface area of  $250 \text{ m}^2 \text{ g}^{-1}$ , and an appropriate amount of isopropyl alcohol (IPA) on the gas-diffusion layer. The air electrode with both the gas-diffusion layer and the active layer was finally sintered at 360 °C for 30 min under a pressure of  $80 \text{ kg cm}^{-2}$ . The thickness of the air electrode was 0.4 to 0.6 mm. The zinc powder gels were prepared according to the following formulation: 67 wt.% Zn powder, 1 wt.% gelling agent (Carbopol 940), 32 wt.% KOH, and some metal additives.

Solid-state Zn–air cells with an alkaline composite PEO–PVA–glass-fibre-mat polymer electrolyte, an air cathode, and a Zn gel anode were assembled and tested. The cells were discharged at different constant currents at room temperature or at a specified temperature. The bulk resistances ( $R_b$ ) of cells before and after discharging were measured by means of ac impedance spectroscopy. The electrochemical characteristics of the cell were evaluated with a BAT778 model charge/discharge unit.

## 3. Results and discussion

The ac impedance spectra for the alkaline PEO–PVA–KOH polymer electrolyte films at different temperatures are shown in Fig. 1. Analysis of the spectra yields information about the properties of the blend polymer electrolyte, such as the bulk resistance,  $R_b$ . Taking into account the thickness of the electrolyte films, the  $R_b$  value was converted into ionic conductivity,  $\sigma$ , according to the formula:  $\sigma (\text{S cm}^{-1}) = l(\text{cm})/R_b(\Omega) \times A(\text{cm}^2)$ . Typically,  $R_b$  values for the PEO–PVA–glass-fibre-mat polymer films are of the order of 1–5  $\Omega$ , and are dependent on the contents of KOH and  $\text{H}_2\text{O}$  in the films. The corresponding values of the ionic conductivity are around  $10^{-2} \text{ S cm}^{-1}$ . The ac impedance spectra for PEO–PVA polymer electrolyte films containing a glass-fibre-mat support were obtained at room temperature. Typical impedance spectra for films with and without a glass-fibre-mat matrix are shown in Fig. 2. The ionic conductivity values of PEO–PVA–glass-fibre-mat composite polymer electrolytes of different composition are listed in Table 1.

Scanning electron micrographs of the PEO–PVA polymer electrolyte films are shown in Fig. 3. The surface morphology of film has a micro-porous structure. The film consists of many small pores with a dimension of about 0.1–0.2  $\mu\text{m}$ , as shown in Fig. 3(a). The film may form a three-dimensional network structure with the glass-fibre-mat support, which allows more KOH electrolyte to be entrapped in the composite polymer matrix, and also enhances the mechanical strength and stability.

High ionic conductivity is not totally sufficient to render a polymer electrolyte suitable for practical battery applications. In cyclic voltammetric studies, the sweep potential

Table 1  
Conductivity ( $\text{S cm}^{-1}$ ) of PEO–PVA–glass-fibre-mat polymer electrolytes of different compositions, at a constant 50% relative humidity

$T$ (°C)	Ratio	
	PEO:PVA = 5:5	PEO:PVA = 7:3
30	0.0475	0.0197
40	0.0492	0.0243
50	0.0524	0.0277
60	0.0540	0.0344
70	0.0580	0.0510

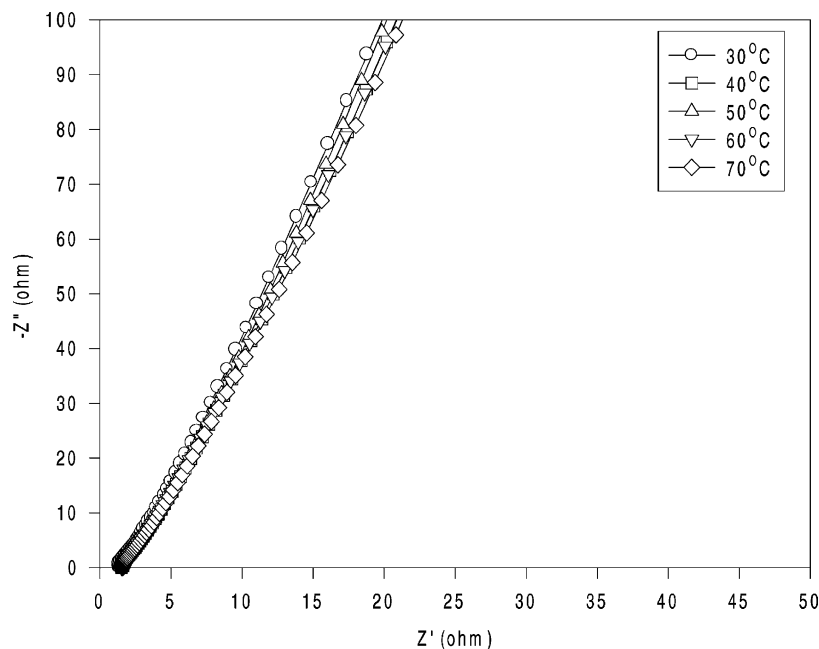


Fig. 1. The ac impedance spectra for composite PEO-PVA polymer electrolyte at different temperatures.

was first scanned in the negative-going direction and then reversed. The electrochemical stability window, defined as a potential region where no appreciable faradaic current flows, is limited in its cathodic and anodic parts, where the reduction and oxidation of the composite polymer electrolyte and  $\text{OH}^-$  ions can take place. A broad electrochemical stability window is important for the practical use of these films. A cyclic voltammograms in the  $-1.5$  to  $+15$  V range for the PEO-PVA polymer electrolyte and the other two types of separator are shown in Fig. 4. The stability of the composite polymer electrolyte at the interface with the stainless-steel

electrode is limited by potentials of about  $+1.2$  and  $-1.2$  V, which gives a window of about 2.4 V. It is obvious that the polyethylene PE/polypropylene (PP) and cellulose separators have much narrower electrochemical stability windows, as shown in Fig. 4. The alkaline composite PEO-PVA-glass-fibre-mat polymer electrolyte demonstrates excellent mechanical strength and electrochemical stability. It is a strong candidate for application in alkaline Zn-air battery.

The discharge curves of Zn-air cells with different separator materials and a composite PEO-PVA polymer electrolyte

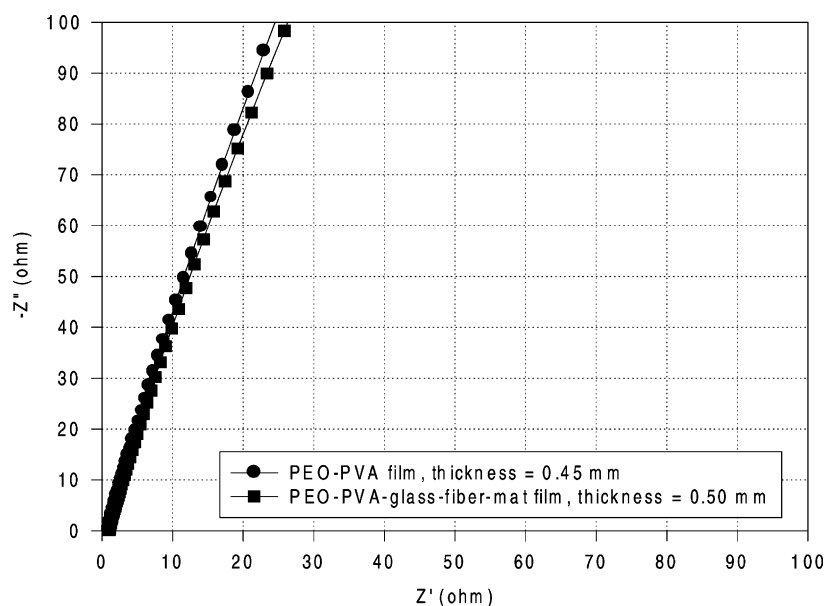


Fig. 2. Comparison ac impedance spectra for PEO-PVA polymer electrolyte film with and without glass-fibre-mat at room temperature.

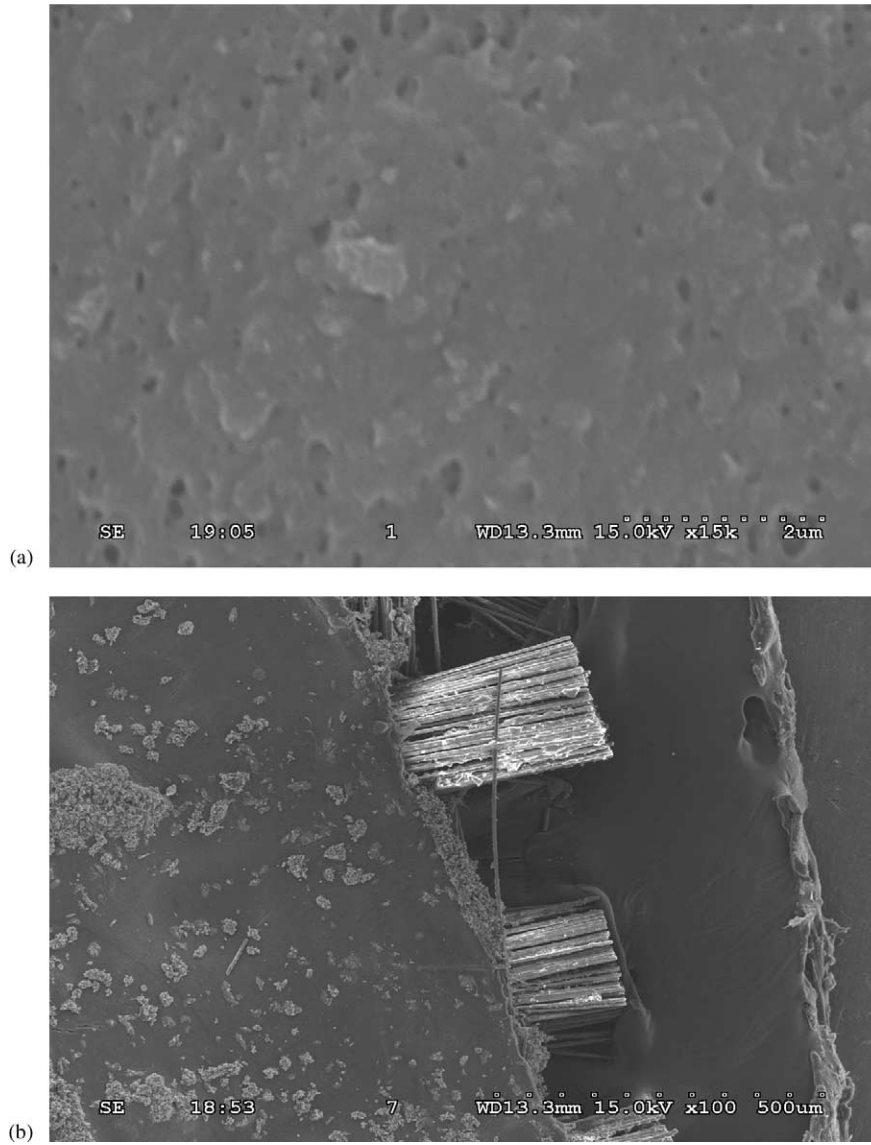


Fig. 3. SEM microphotographs for composite PEO-PVA polymer electrolyte films: (a) top view of film; (b) side view of film.

film are given in Fig. 5. The cell with the polymer electrolyte displays the highest capacity, viz. 1305 mAh (theoretical capacity: 1560 mAh, utilization of zinc = 83.65%) at the  $C/10$  rate at 25 °C. By contrast, the utilization of conventional Zn-air batteries with PE/PP and cellulose separators is 75

and 78%, respectively. The experimental results for Zn-air cells with different types of separator and solid polymer electrolytes are listed in Table 2. The cell with the solid polymer electrolyte has higher capacity and higher utilization of material on account of the much smaller pore size

Table 2

Results for different Zn-air cells under a constant current condition (cell dimensions: 2 cm × 3 cm, area = 6 cm<sup>2</sup>)

Parameter	Cell		
	Zn-air with PP/PE separator	Zn-air with cellulose separator	Zn-air with PEO-PVA polymer electrolyte
Theoretical capacity (mAh)	1560	1560	1560
Discharge current (mA)	150	150	150
Discharge time (hr)	7.8	8.2	8.7
Real capacity (mAh)	1170	1230	1305
Utilization (%)	75	78.85	83.65

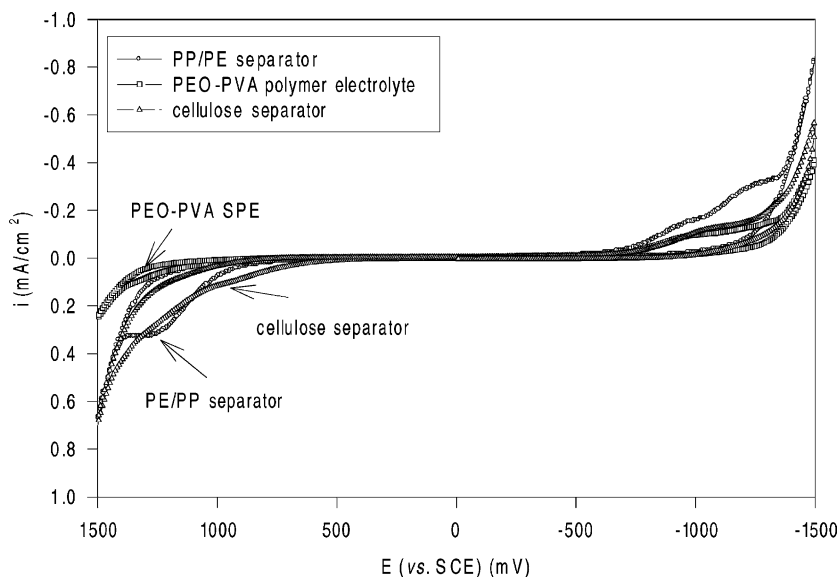


Fig. 4. Cyclic voltammogram for composite PEO–PVA polymer electrolyte film and PE/PP and cellulose separators at scan rate of 1 mV/s at 25°C.

(0.1–0.2  $\mu\text{m}$ ) within the composite PEO–PVA polymer matrix compared with that in PE/PP and cellulose separators. The conventional Zn–air cell using a PE/PP separator, or a cellulose with a pore size of about 10–20  $\mu\text{m}$ , is much more easily short-circuited when it is under a high discharge rate. This is due to the much larger pore size and non-uniform pore size distribution within the PE/PP separator. Discharge curves for a solid-state Zn–air cell with a composite PEO–PVA polymer electrolyte at different discharge rates are shown in Fig. 6. The utilization of zinc material is

about 82–92% at discharge rates of C/5 to C/20, as listed in Table 3.

Discharge curves for a solid-state Zn–air cell with a composite PEO–PVA polymer electrolyte at different temperatures are presented in Fig. 7. The utilization of zinc material is about 75–83% over the temperature range of 0–50 °C at C/10 rate, as listed in Table 4.

The results of an ac impedance analysis for a solid-state Zn–air cell with a PEO–PVA–glass-fibre-mat polymer electrolyte at different temperatures are shown in Fig. 8. The

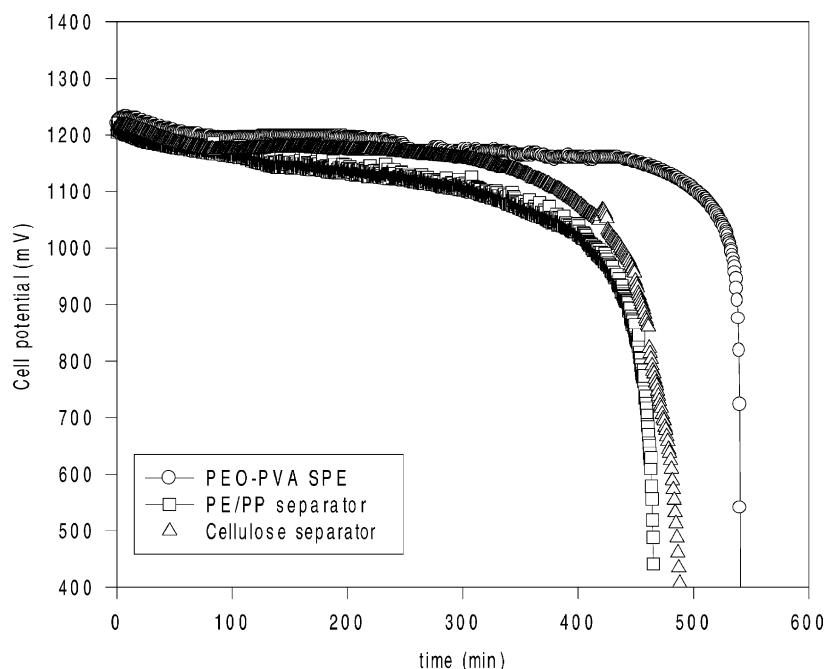


Fig. 5. The discharge curves of solid-state Zn–air cells with PEO–PVA SPE and Zn–air with different separators at C/10 rate at 25°C.

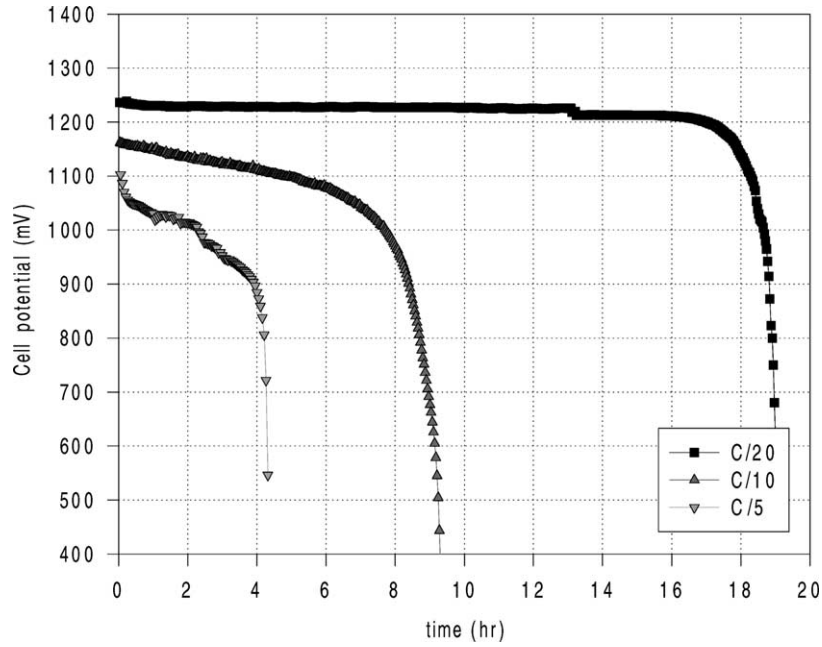


Fig. 6. The discharge curves of solid-state Zn-air cells with composite PEO-PVA polymer electrolyte at varied discharge rates at 25°C.

Table 3

Results for a solid-state Zn-air cell at different discharge rates (cell dimensions: 2 cm × 3 cm, area = 6 cm<sup>2</sup>; PEO:PVA = 5.5)

Parameter	Discharge rate		
	C/5	C/10	C/20
Theoretical capacity (mAh)	1560	1560	1560
Discharge current (mA)	300	150	75
Discharge time (h)	4.31	9.35	19.08
Real capacity (mAh)	1293	1402.5	1431
Utilization (%)	82.88	89.90	91.37

Table 4

Results for a solid-state Zn-air cell at different temperatures (cell dimensions: 2 cm × 3 cm, area = 6 cm<sup>2</sup>; PEO:PVA:KOH:H<sub>2</sub>O = 20:20:30:30 wt.%)

Parameter	Temperature (°C)		
	0	20	50
Theoretical capacity (mAh)	1560	1560	1560
Discharge current (mA)	150	150	150
Discharge time (h)	7.8	8.2	8.7
Real capacity (mAh)	1170	1230	1305
Utilization (%)	75	78.8	83.65

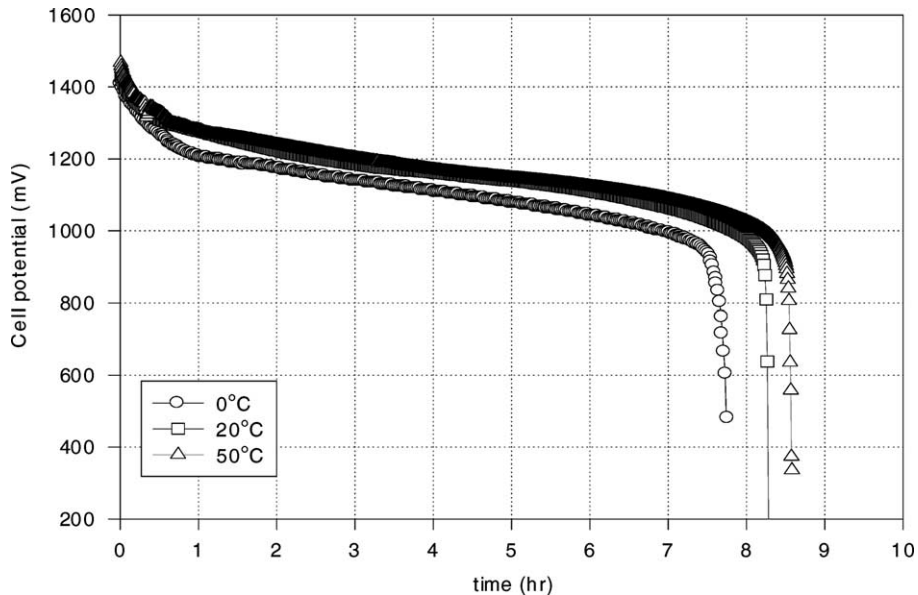


Fig. 7. The discharge curves of solid-state Zn-air cells with PEO-PVA-glass-fibre-mat polymer electrolyte at various temperatures at C/10 discharge rate.

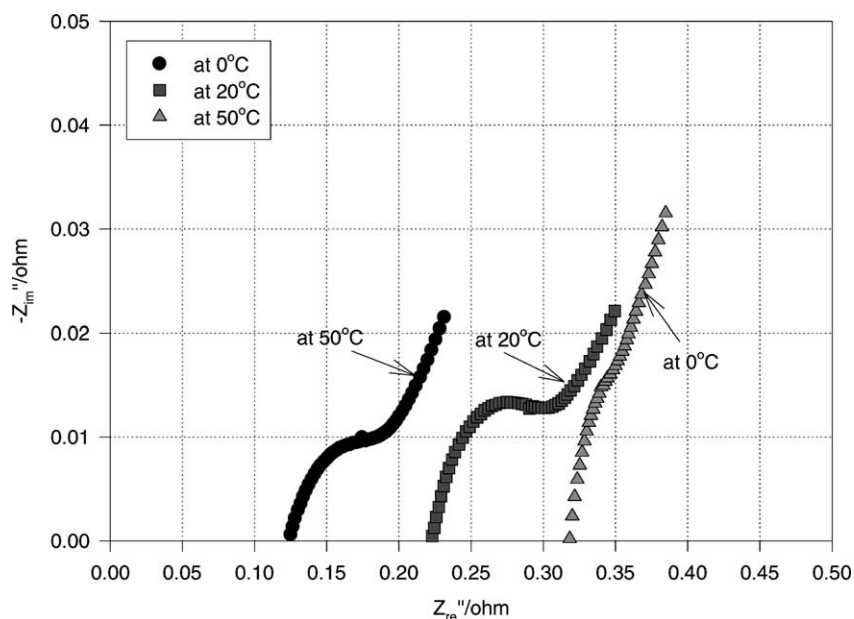


Fig. 8. The result of ac impedance analysis of solid-state Zn–air cells with PEO–PVA–glass-fibre-mat SPE at various temperatures at  $C/10$  rate.

Table 5

Results of ac impedance analysis of a solid-state Zn–air cell at different temperatures (cell dimensions:  $2\text{ cm} \times 3\text{ cm}$ , area =  $6\text{ cm}^2$ )

Impedance ( $\Omega$ )	Temperature ( $^{\circ}\text{C}$ )		
	0	20	50
$R_b$	0.321	0.225	0.125

bulk impedance,  $R_b$ , of the cell was determined from a Nyquist plot over the range  $0$ – $50\text{ }^{\circ}\text{C}$ . The bulk impedance is between  $0.125$  and  $0.32\text{ }\Omega$  over the temperature range of  $0$ – $50\text{ }^{\circ}\text{C}$  at  $C/10$  rate, as listed in Table 5.

#### 4. Conclusions

Alkaline composite PEO–PVA–glass-fibre-mat polymer electrolytes have been prepared by a solvent casting method. The characteristic properties of the electrolytes have been studied by means of scanning electron microscopy, cyclic voltammetry and ac impedance spectroscopy. The conductivity of the electrolyte film is around  $0.01\text{ S cm}^{-1}$  at room temperature, it depends on the composition of the electrolyte. It is concluded that the composite polymer electrolytes have excellent mechanical strength and electrochemical stability ( $\pm 1.2\text{ V}$ ). Solid-state Zn–air batteries have been assembled and examined. The results demonstrate that the electrochemical performance of Zn–air cells with composite polymer electrolytes is much better than that of conventional cells with PE/PP or cellulose separator. The alkaline composite PEO–PVA–glass-fibre-mat polymer electrolyte shows promise for application in Zn–air batteries.

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