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Effect of Polyaniline on the Ionic Conductivity of PVA/NaCl Composite Electrolyte Membranes

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Abstract. This study investigates the effect of polyaniline (PANI) on the ionic conductivity and performance of polyvinyl alcohol (PVA)/sodium chloride (NaCl) composite electrolyte membranes for application in aluminum-air batteries. PVA/NaCl/potato starch (PS) membranes with varying PANI concentrations (0, 1, 1.5, and 2 g) were prepared and characterized. Tensile strength tests revealed that increasing PANI content led to increased brittleness and decreased elastic properties of the membranes. Electrochemical impedance spectroscopy showed that adding 2 g of PANI resulted in the highest ionic conductivity of 1.69 mS/cm. Galvanostatic discharge tests demonstrated that the membrane with 1.5 g of PANI exhibited the longest operational time of 677 s at 1 mA and the highest initial voltage of 1.42 V. The battery with 1.5 g of PANI in the electrolyte membrane also achieved the highest electrical capacity of 0.188 mAh. However, excessive PANI content (2 g) led to a decrease in battery performance. The results suggest that the optimal PANI concentration for enhancing the performance of PVA/NaCl/PS electrolyte membranes in aluminum-air batteries is 1.5 g. This study highlights the potential of PANI as an additive for improving the ionic conductivity and performance of composite electrolyte membranes in Al-air batteries.

Keywords: Al-air Battery, Composite, Conductivity, PANI, Potato Starch

INTRODUCTION

The creation of effective and environmentally friendly batteries has become essential when the need for energy keeps growing, and worries about its effects are becoming more pressing. Using composite materials to improve battery performance is one possible strategy. The use of a composite material as electrodes in a battery system that comprises polyvinyl alcohol (PVA), sodium chloride (NaCl), potato starch (PS), and polyaniline (PANI) is the main focus of this study. PVA is an organic binder to increase mechanical strength. Therefore, PVA is the main ingredient in battery electrolytes (Wong & Aziz, 2007). The electrolyte or ion conductor serves as a pathway for transferring the ions generated by the electrodes (Wahyusi *et al*., 2023)

The maximum conductivity of 15.0 S/cm was obtained in the HCl-PANI-PVA composite conductive coating (Wang, 2012). Through electrospinning a blend of polyaniline (PANI) and PEO, MWNTs are combined to create conducting composite nanofibers (Shin *et al*., 2008). The maximum conductivity at a certain oxidant to monomer molar ratio of 1.20–1.25

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validated that PANI is a conductor (Ali *et al.*, 2009). Electrical properties of polyaniline and cobalt ferrite nanocomposites synthesized via hydrothermal route, revealing polyaniline's superior conducting mechanism (Tanrıverdi *et al.*, 2011). The synthesis of PVA/PANI films for supercapacitor applications revealed increased specific capacitance with thickness and stability for over 20,000 cycles (Patil *et al.*, 2011).

Metal-air batteries (MABs) are a sustainable, low-cost energy storage solution, discussing their advantages, applications, and technological advancements (Ahuja *et al.*, 2021). The performance of the composite membrane was assessed in a lithium-air cell, showing promising results for potential use in high-energy-density batteries (Safanama *et al.*, 2014). The carbon air battery demonstrated an attractive peak power density of 279.3 mW cm^{-2}. It showed high energy density and power output, with a small stack of two batteries operating continuously for 200 minutes (Yang *et al.*, 2015). Adding WSG to the 3.5% NaCl electrolyte increased the current density from 13.24 to 19.33 mA cm^{-2}, enhancing battery performance (Mayilvel Dinesh *et al.*, 2015). The use of KOH electrolytic solution in an air battery was found to produce a higher voltage compared to NaCl solution (Oguntosin & Akindele, 2021). The aluminum alloy Al-6061 produces more hydrogen and loses more mass through corrosion than pure aluminum (Katsoufis *et al.*, 2020). Zinc-air flow batteries with increased KOH content can increase higher ionic conductivity and smaller pore size (Sankaralingam *et al.*, 2022). Batteries that use Zn/Air have the potential to become economically viable due to their improved recyclability, and it is important to take into account the environmental effects of battery production (Santos *et al.*, 2020). Flexible rechargeable zinc-air battery retains over 92.7% capacity and 87.2% energy density when the temperature decreases from 25 to -20 °C (Pei *et al.*, 2020). Solid-state zinc-air battery with a three-electrode structure using a sodium polyacrylate (PAA-Na) hydrogel as the electrolyte, this new battery demonstrates high power density and longevity, making it suitable for flexible electronic devices (Zhao *et al.*, 2020).

This study is expected to significantly advance the creation of more effective and sustainable batteries by providing a thorough understanding of the characteristics of the PVA/NaCl/PS/PANI composite material. Future battery technologies that are both environmentally friendly and able to fulfill the world's expanding energy demands may be made possible by the findings of this study.

MATERIALS AND METHOD

Materials

The chemical reagents and materials, including PVA, fully hydrolyzed 8.43866.1000 (MW of approx. 60000 g/mol), NaCl (99%), PS 101252 Potato Starch ($C_6H_{10}O_5$,) were sourced from Merck, and PANI were sourced from a local store (Inovasi Teknologi Nano (ITNANO) -NRE Lab) used in this investigation.

Preparation of Solid Electrolyte Membrane

PVA solution was prepared by adding 4 g of PVA to 100 mL of distilled water and heating the mixture while stirring at 60-80°C for approximately 2 h. This solution was used as an electrolyte, and 1.5 g of NaCl was dissolved in 25 mL of distilled water. The NaCl solution was then combined with the PVA solution and stirred until homogeneous. A PS solution with a 6% concentration of PVA was added to 25 mL of distilled water and mixed with the PVA/NaCl solution at a temperature of 60-80°C for 1 h. Finally, 1 g of PANI was added to the homogeneous PVA/NaCl/PS solution, which was then stirred for 1 h at a temperature of 60-80°C until it became a thick solution. The solution was then poured into tensile and air battery test molds. Kindly follow these guidelines for the PANI variances (1.5 and 2 g). The tensile test was conducted using a D368 Type 5 tensile testing machine at a crosshead speed of 20 mm/min.

Electrical properties are acquired through experimentation utilizing a Corrtest 100E potentiostat with a frequency range of 10 µHz to 1 MHz. Measuring precision was maintained with a 0.1% × full range accuracy, 10 mV potential resolution, and 100 fA current resolution using a three-electrode configuration. The impedance of a circuit is the measure of its resistance to the flow of alternating current (AC), symbolized by |Z| and determined using Eq. (1). It is a complex quantity made up of both resistance (Z_e) and reactance (Z_{im}), which is essential for analyzing electrical circuits, particularly in AC circuits, as it affects how the circuit reacts to various frequencies.

$$|Z| = \sqrt{{Z_{r_e}}^2 + {Z_{im}}^2} \quad (1)$$

Ionic conductivity was calculated using Eq.(2).

$$\sigma = \frac{L}{R_b \times A} \quad (2)$$

Where L is the electrolyte membrane thickness (0.5 cm), Rb is the bulk resistance obtained from the Nyquist plot intercept, and A is the electrode area (2 cm^2).

It is necessary to perform galvanostatic discharge to showcase the effectiveness of Al-air batteries, which utilize aluminum as the anode and carbon as the cathode. This demonstration involves using a membrane composed of PVA/NaCl/PS/PANI. The primary objective is to highlight the significant influence of PANI concentration on the overall capacity.

RESULTS AND DISCUSSION

Tensile Strength

This study evaluated the tensile strength of PVA/NaCl/PS samples infused with PANI in varying concentrations (0, 1, 1.5, and 2 g). According to the findings, the sample's tensile strength was considerably decreased by the addition of PANI. The sample without the PANI combination has the highest tensile strength, 14.49 MPa, as shown in Figure 1. Samples mixed with PANI have lower tensile strength as the PANI composition increases. The tensile strength of the sample with 2 g of PANI was the lowest, amounting to 6.5 MPa.

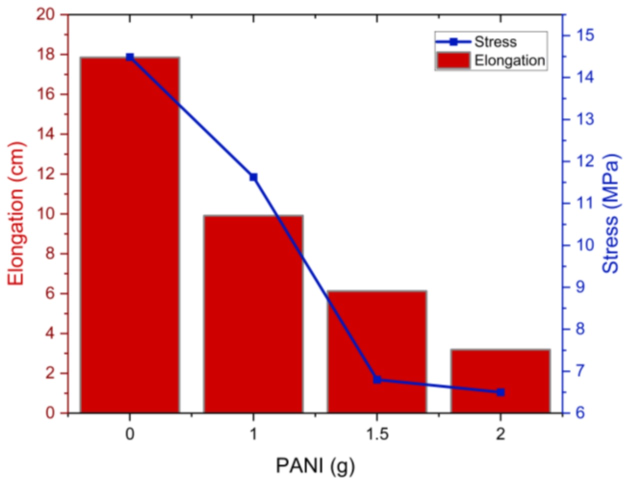

Fig. 1: Tensile strength of PVA/NaCl/PS/PANI

The reason is that as the concentration of PANI in the sample increases, as demonstrated in Figure 2 (b), the sample becomes more brittle. Conversely, samples without PANI, as depicted in Figure 2 (a), show more ductility.

Electrochemical Impedance Spectroscopy (EIS)

The Nyquist plot of battery impedance

with the solid PVA/NaCl/PS electrolyte and PANI variations (0, 1, 1.5, 2 g) displayed in Figure 3 operates within a frequency range of 10 mHz to 10 kHz, with a minimum frequency of 10 mHz and a maximum frequency of 10 kHz. The resistance fluctuation curves for both real (Z_{re}) and imaginary (Z_{im}) components in the electrolyte decrease as the amount of PANI increases, resulting in an improved semicircular curve. This is because PANI is a conductive material, so increasing PANI in the solid electrolyte causes faster ion transfer in the battery. The ionic conductivity of each membrane can be determined by utilizing the impedance value and cross-sectional area of the electrode.

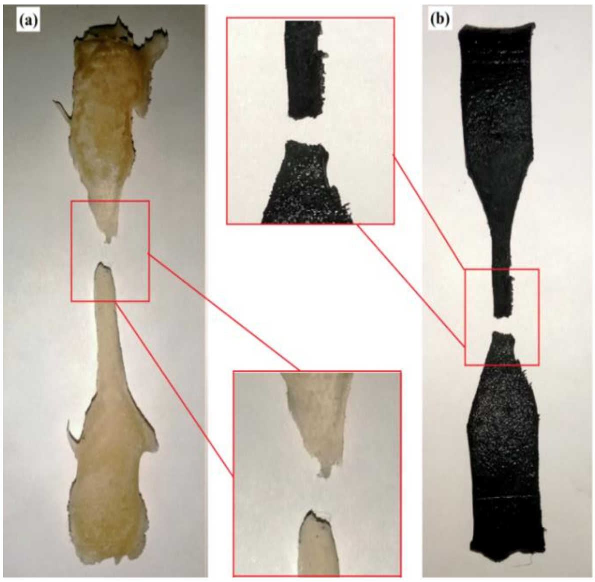

Fig. 2: Specimen PVA/NaCl/PS form after tensile testing, (a) without adding PANI, (b) with 2 g PANI addition

Figure 4 shows the cyclic voltammetry of a PVA/NaCl/based solid electrolyte at a voltage range of -0.2 to 1.5 V. Adding 2 of g PANI shows the highest peak oxidation current, specifically 1.4 x 10^{-2} A. The peak oxidation current decreases in the following order: 1.5 g, 1 g, and 0 g, with their respective current values of 6.3 x 10^{-3} A, 4.4 x 10^{-3} A, and 6.4 x 10^{-4} A. Adding 2 g of PANI extends the length of the oxidation process.

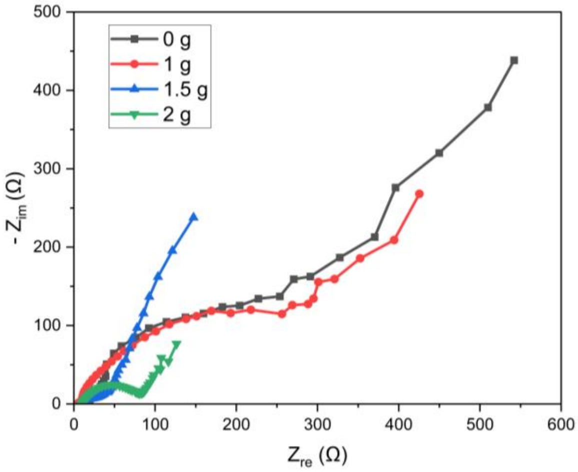

Fig. 3: Nyquist plot of PVA/NaCl/PS/PANI

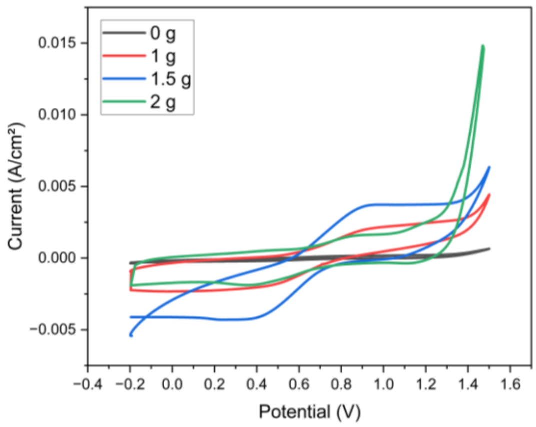

Fig. 4: Cyclic voltammetry plot of PVA/NaCl/PS/PANI

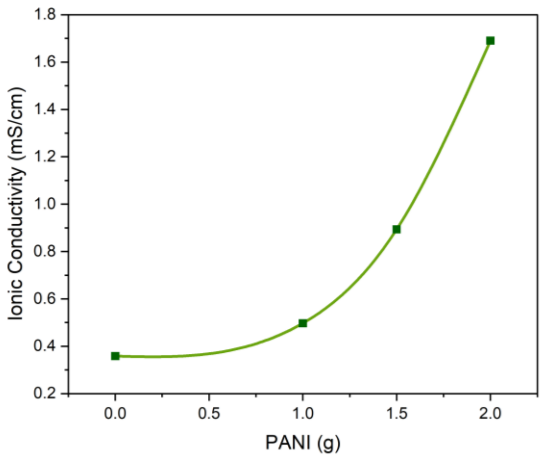

Fig. 5: Ionic conductivity of PVA/NaCl/PS/PANI solid electrolyte, Al-air battery calculated based on Eq. 2

Based on Figure 5, batteries with electrolyte membrane variations of 2 g of

PANI have the highest conductivity of 1.69 mS/cm. Compared with membranes without PANI mixture, there is a significant change in conductivity. Therefore, based on this, PANI can help improve the conductivity of air battery membranes (Yu *et al.*, 2019, Indica & Indica, 2013).

Table 1. Research development on increasing the ionic conductivity of solid polymer electrolytes (SPE)

Electrolyte	Conductivity (mS/cm)
PVA/KCL/GL/CQD (Ridwan *et al.*, 2025)	0.84
PVA/TEOS/HCl/CA (Ridwan, Agusta, *et al.*, 2024)	2.78
PVA/KOH/GL/NCC Kapok (Ridwan, Febriyan, *et al.*, 2024b)	0.068
PVA/KOH/GL/NCC Paper (Ridwan, Febriyan, *et al.*, 2024a)	0.512
PVA/CS/XG/AC (Aprilman *et al.*, 2025)	0.0117
PVA/NaCl/PS/PANI (This research)	1.69

This study compared various solid polymer electrolytes (SPEs) with different compositions regarding their ionic conductivity, as summarized in Table 1. The electrolyte developed in this research, composed of PVA/NaCl/PS/PANI, achieved a conductivity of 1.69 mS/cm, indicating promising ionic transport properties.

Al-air Battery Discharging Performance

The discharging performance of an air battery with carbon as the cathode and aluminum as the anode can be affected by increasing PANI in the solid electrolyte, as demonstrated in Figure 6.

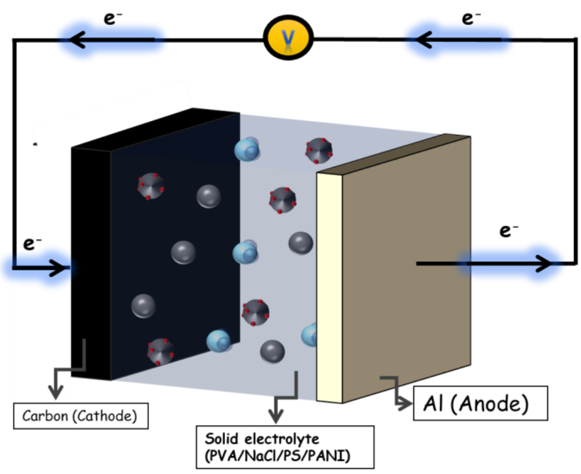

Fig. 6: Al-air battery with PVA/NaCl/PS and PANI variation

The time required for discharging a battery without incorporating PANI in the solid electrolyte is depicted in Figure 7 (a) and begins at 1.26 V, lasting for 295.9 s. The discharge duration and voltage drop to 136.26 s and 1.24 V, respectively, with a discharge current of 2 mA. The battery voltage decreases over time during discharging, eventually reaching 0 V. The relationship between amperage and battery drain rate can be observed through the 5 mA and 10 mA discharge experiments, where a higher amperage results in a faster battery drain. The addition of 1 g of PANI to the solid electrolyte, as demonstrated in Figure 7 (b), resulted in an increase in the discharge time to 585.5 s at a current of 1 mA, as well as an increase in the initial voltage to 1.35 V, which then continued to decrease at 2, 5, and 10 mA. 1.5 g of PANI has an effect, as seen in Figure 7 (c). Among solid electrolytes with different PANI variants, this one has the longest discharge duration and beginning voltage—at 1 mA, the discharge lasts 677 s and has an initial value of 1.42 V. At 2 mA, the discharge time is significantly shorter. This trend holds for 5 and 10 mA discharge currents. Figure 7 (d) shows that the addition of 2 g PANI decreases battery performance,

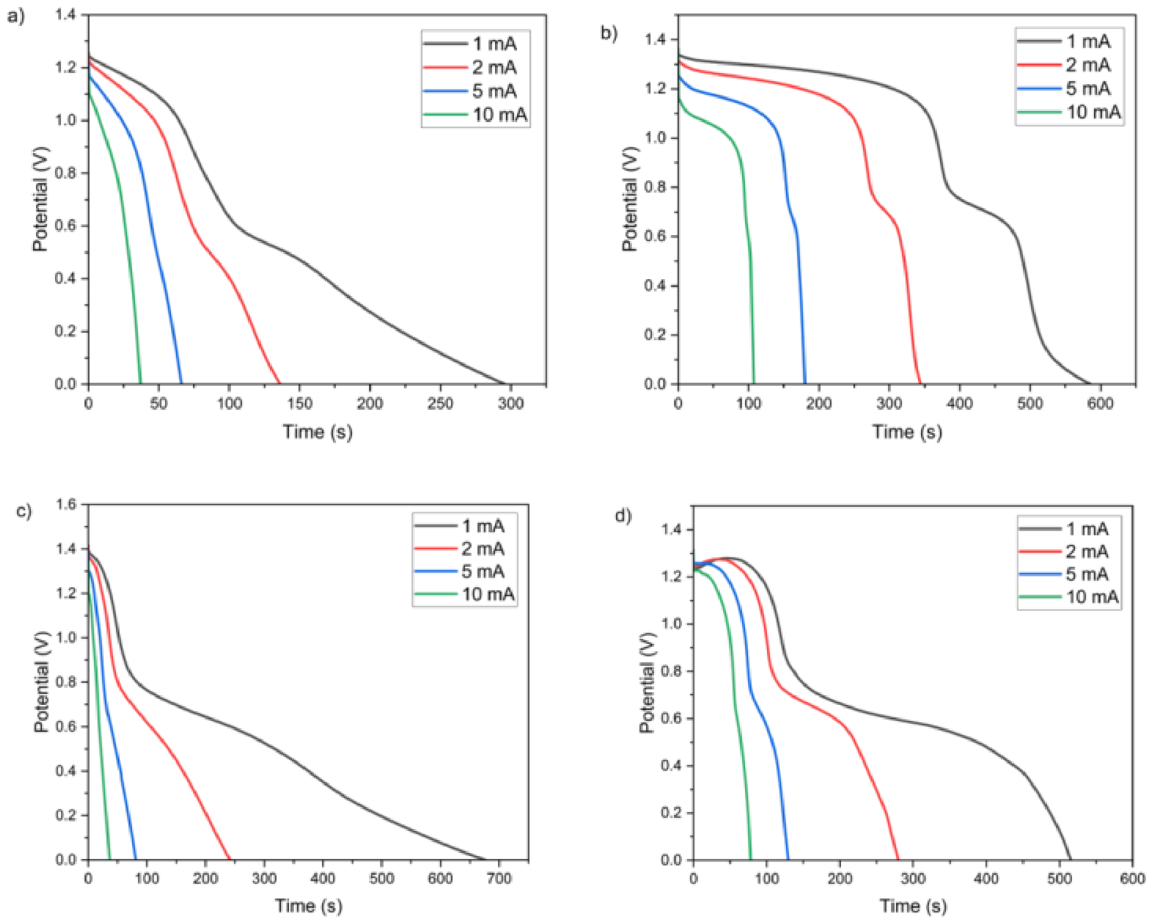

Fig. 7: Galvanostatic discharge test of Al-air battery with membrane a) PVA/NaCl/PS, b) PVA/NaCl/PS/1 g PANI, c) PVA/NaCl/PS/1.5 g PANI, d) PVA/NaCl/PS/2 g PANI, at constant amperes varying 1 mA, 2 mA, 5 mA and 10 mA

as seen in the discharge time of 515.5 s at 1 mA with an initial voltage that also decreases to 1.25 V. The initial voltage is 1.24 V at 2 mA for 279.83 s and continues to decrease at 5 mA and 10 mA. This research demonstrates that PANI concentrations impact battery discharge variables, but excessive amounts of PANI can diminish the battery's electrical capacity.

Figure 8 concludes the discharging process, showing that a battery with a solid electrolyte containing 1.5 g PANI has the highest electrical capacity of 0.188 mAh. These findings reveal that PANI can influence the maximization of electrical capacity (Raghavan *et al*., 2021).

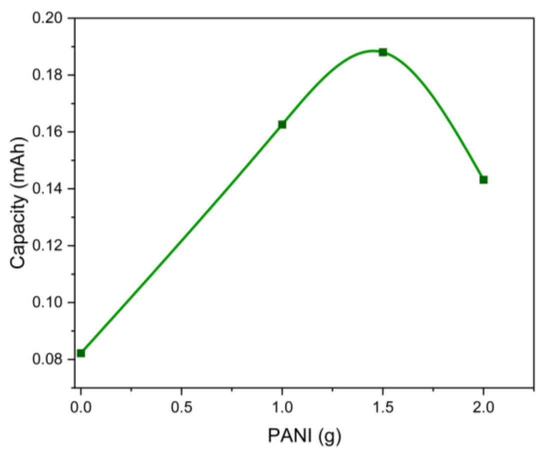

Fig. 8: Batteries capacity of PVA/NaCl/PS/PANI Al-air battery

CONCLUSIONS

This research shows the effect of adding PANI to the electrolyte membrane of an air battery with aluminum as the anode and carbon as the cathode. The tensile strength test results indicate that incorporating PANI into the electrolyte membrane increases its brittleness, decreasing its elastic properties. Adding 2 g of PANI increased ionic conductivity by 1.69 mS/cm. Furthermore, adding 1.5 g of PANI enhanced the longest operational time to 677 s at 1 mA, and the highest initial voltage was recorded at 1.42 V. The addition of 1.5 g of PANI to the PVA/NaCl/PS membrane demonstrates the most optimal performance for application in air batteries, as indicated by this research.

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NOMENCLATURE

$\|Z\|$	:	Impedance [Ω]
Z_{r_e}	:	Impedance real [Ω]
Z_{im}	:	Impedance imaginer [Ω]
L	:	Electrolyte membrane thickness [cm]
Rb	:	Bulk resistance [Ω]
A	:	Electrode area (cm^2)

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