



# Acrylamide-derived freestanding polymer gel electrolyte for flexible metal-air batteries



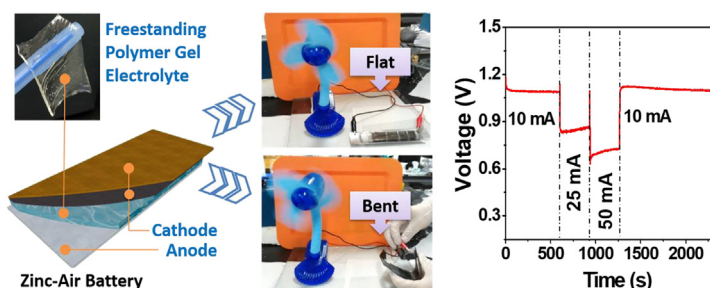
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## HIGHLIGHTS

- Developed ion-conductive freestanding polymer gel electrolyte with  $\sigma = 0.33 \text{ S cm}^{-1}$ .
- Enabled Zn-air batteries with fully retained performance at a bent angle down to  $60^\circ$ .
- Achieved 37% longer cycle life for Zn-air batteries than other electrolytes.
- Facilitated Al-air battery to deliver high areal specific capacity of  $20 \text{ mAh cm}^{-2}$ .

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

Robust freestanding polymer gel electrolytes (PGEs) are fabricated *via* a facile approach and used for flexible zinc-air (Zn-air) and aluminium-air (Al-air) batteries. The fabrication involves an ultraviolet light-initiated free radical polymerization of acrylamide using N,N'-methylenebis (acrylamide) as crosslinker to form a partially crosslinked polyacrylamide, and the soaking of the resultant polymer in a potassium hydroxide aqueous solution or a saline. With their merits of good flexibility, high ionic conductivity ( $\sigma = 0.33 \text{ S cm}^{-1}$ ), easy fabrication and scalability, these freestanding PGEs qualify as superb candidates to enable high performance flexible metal-air batteries. The Zn-air batteries show no noticeable performance degradation at a bending angle down to  $60^\circ$ , delivering a power density of  $39 \text{ mW cm}^{-2}$  and a stable voltage profile over 50 h of continuous cycling (1 h per cycle) with a discharge and charge potential of 1.2 and 2.0 V, respectively. The flexible Al-air battery assembled using a neutral pH PGE and a household aluminium foil anode gives a high areal specific capacity of up to  $20 \text{ mAh cm}^{-2}$ .

## 1. Introduction

The ever-increasing demand on safer and cost-effective technologies for large scale energy storage is putting pressures on the lithium-ion batteries using flammable electrolyte with additional concerns of fast

lithium depletion and high cost of recycling [1–4]. Zinc-air (Zn-air) battery is emerging as a promising alternative due to its high specific energy (up to  $1086 \text{ Wh kg}^{-1}$ ), low cost and environmental benignity [1,5–9]. On the other hand, rapid advancement of flexible and wearable devices for the next-generation electronics [10,11] is demanding an

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accompanied shift in the design and fabrication of the power sources from those conventional bulky and stiff ones to their thin and flexible counterparts [12–16]. To accommodate this shift, liquid electrolyte in the prevailing Zn-air batteries with the risks of leaking out and issues of water evaporation [17,18] would need to be replaced by viscous polymer pastes, such as polyethylene oxide (PEO), polyvinyl alcohol (PVA), or their blends with a “non-leaking” nature [19,20]. Commonly, a piece of glass fiber mat is required to confer mechanical stability in a working cell. Consequently, it increases the weightage of electrochemically inactive components and thus compromises the energy density of the Zn-air battery. It remains a challenge to fabricate robust freestanding solid-state electrolyte for high-performance thin and flexible Zn-air batteries [17,21,22].

Thin polyacrylic acid (PAA) polymer films are able to absorb potassium hydroxide (KOH) aqueous solution to yield a polymer gel electrolyte (PAAK-OH PGE), as reported in zinc/manganese oxide (Zn/MnO<sub>2</sub>) and Zn-air primary cells [23]. Later, by immersing a membrane that was cast from a blend of PAA and PVA into 32 wt% of KOH aqueous solution, freestanding PGE with an ionic conductivity up to 0.301 S cm<sup>-1</sup> was obtained and applied in Zn-air and Al-air batteries [24]. Nevertheless, the PAAK-OH PGE in the former was found not able to retain its flexibility at a crosslinking degree greater than 1.0%, excluding their use in flexible batteries that require stringent mechanical strength. The binary composites in the latter complicate the processing, increasing the cost and reliability risks in large area freestanding electrolyte fabrications. PGEs out of a single-polymer are of clear advantages, if their electrochemical performances in the corresponding metal-air batteries can be achieved at a level better or at least on a par with that of its counterpart using binary component PGEs.

Herein, we report a robust freestanding PGE, derived from a highly crosslinked homo-polymer, which enables bendable metal-air batteries with high performance in the absence of conventional auxiliary mechanical supports. The crosslinked polymer, polyacrylamide (PAM), is readily synthesized via an ultraviolet (UV) light-initiated radical polymerization of acrylamide from its aqueous solution using N,N'-methylenebis(acrylamide) (MBAa) as the crosslinkers. Soaking the PAM films in KOH aqueous solution led to the formation of freestanding alkaline PGEs. The ionic conductivity of the freestanding alkaline PGEs was measured with respect to the employed KOH concentration or molar ratio of crosslinkers (*determining the swelling ratio of the film*) using impedance spectroscopy. Freestanding PGEs with high ionic conductivity and mechanical strength were obtained by soaking PAM films synthesized at 0.2 mol % of (w.r.t. acrylamide) MBAa in 6 M KOH aqueous solution, and found particularly suitable for Zn-air batteries. As a proof of concept, a flexible Zn-air battery was assembled to power a small electrical fan at the flat and bent states of the battery, respectively. The highly crosslinked PAM film was also found compatible with aqueous saline, forming solid-state, free-standing and flexible neutral pH PGE for flexible aluminum-air (Al-air) batteries.

## 2. Experimental

### 2.1. Chemicals and materials

Acrylamide, N,N'-methylenebis(acrylamide), ammonium persulfate (APS), sodium chloride, potassium bromide, Nafion<sup>®</sup> ethanol solution and poly(acrylic acid) (avg. Mw: 1,250,000) were Sigma-Aldrich products. Potassium hydroxide (KOH, assay 98%) was purchased from Merck. All chemicals were used as received without further purification. Zinc foil (0.25 mm thick) and 10 BN-carbon papers were purchased from Alfa Aesar and SGL Carbon, respectively. Nickel foam, copper mesh, and customized CR2032-stainless steel coin cell casings (one side was drilled with 19 small holes) were sourced from Latech Scientific Supply Pte. Ltd. in Singapore. Aluminum foil was of household grade, purchased from a local supermarket (NTUC FairPrice). C-CoPAN900 catalyst was synthesized from electrospinning with

subsequent thermal treatments as reported previously [25].

### 2.2. Synthesis of alkaline polymer gel electrolyte (PGE)

The synthesis of polyacrylamide (PAM) in this work was following a well-established UV light-initiated radical polymerization protocol [26,27]. Typically, 1.0 g of acrylamide monomer was dissolved in 5.0 mL of deionized (DI) water, and subsequently purged with dry nitrogen gas (N<sub>2</sub>) for 20 min. In a separate vial, 4.3 mg of MBAa crosslinker (0.2 mol % of the monomer) and 6.4 mg of APS initiator (0.2 mol % of the monomer) were dissolved in 5.0 mL of DI water. The two solutions were mixed thoroughly for 1 min prior to cast into a Teflon petri dish, subject to immediate irradiation provided by a UV curer (Dymax Flood, 2000) for 45 min of UV light-initiated free radical polymerization (Scheme S1). After vacuum drying, the obtained PAM film was soaked into 6 M KOH aqueous solution to form freestanding alkaline PGEs. The quality of PGEs is controlled by fine-tuning the molar ratio of MBAa to acrylamide monomer in the PAM synthesis.

### 2.3. Characterisation methods

Fourier transform Infra-red (FTIR) spectra were recorded on a Perkin Elmer Spectrum 2000 from the potassium bromide (KBr) pellets of PAM or PAM/KOH. Electrochemical impedance spectroscopy data was collected on a potentiostat/galvanostat instrument (Autolab) over a frequency range of 0.1–10 kHz at an amplitude voltage of 10 mV. The PGE samples were cut into desired dimensions and placed onto a customized jig with two parallel electrodes spaced 1.5 cm apart. Elemental Analysis (EA) data was collected on a ThermoFisher Scientific FlashEA 1112.

### 2.4. Assembly and electrochemical characterisation of Zn-Air coin cells

Zn-air coin cells were assembled in ambient environment, and the components used include a piece of polished zinc as anode, PAM-based alkaline PGE, catalyst-loaded carbon paper air-cathode, nickel foam current collector, customized CR2032 stainless steel coin cell casings, with the cathode side holding 19 small holes to allow for easy permeation of oxygen (Fig. S1). PAM/KOH PGEs from PAM synthesized with 0.2 mol % of MBAa were cut into circles of right size. Carbon paper and nickel foam were press-punched into the dimension of D = 12.5 mm 12.3 mg of C-CoPAN900 [25] was dispersed into 1.0 mL of diluted Nafion ethanol (1.5 wt%) to form a catalyst ink. 100 μL of the freshly prepared catalyst ink was drop-cast onto the carbon paper and left dry to form the air cathode. The assembly of cells follows the sequence of stainless steel anode casing, Zn anode, PGE, air cathode, nickel foam and the 19-hole stainless steel cathode casing, and the assembled cells were evaluated on a battery tester (MACCOR 4300, USA). As control, Zn-air coin cells using paste electrolyte of commercial PAA dissolved in 6 M KOH were also assembled following the same protocol and tested accordingly.

### 2.5. Assembly of thin film and bendable Zn-Air and Al-Air battery

For thin film Zn-air batteries, Zn foil sheets were used as anode and current collector, with alkaline PAM PGEs having an in-plane dimension of 20 mm × 60 mm. C-CoPAN900 powder was directly and evenly spread onto the surface of the alkaline PAM PGE and pressed gently to obtain a flat surface. A copper mesh was used as current collector at the air cathode side. Thin film Al-air cells were assembled from a similar protocol, except for the use of household aluminum foil at the anode side and a neutral pH PGE prepared from PAM and 10 wt% sodium chloride (NaCl) aqueous solution.

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