



Short communication

Defect free rolling phase inversion activated carbon air cathodes for scale-up electrochemical applications

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ABSTRACT

Scalable production of air cathodes is crucial for applying electrochemical technologies in practical water treatment applications. However, existing fabrication procedures of air cathodes for microbial fuel cells (MFCs) are either complicated or not sufficiently waterproof for larger-scale processes. In this study, an easily implemented low-pressure rolling phase inversion method was developed for preparing scalable, waterproof activated carbon air cathodes. An aminated PVDF (NH₂-PVDF) membrane was synthesized as a new gas diffusion layer (GDL) to avoid defect formation from contacting organic solvent during cathode fabrication. The cathode was easily enlarged to 1000 cm² with a high pressure resistance of 13 ± 0.7 m H₂O height (~1.37 kPa), exceeding the waterproof capability of previously reported air cathodes. The electrochemical performance of the fabricated air cathode was not affected by the additional membrane. MFCs with the NH₂-PVDF cathodes produced a maximum power density of 1010 ± 40 mW m⁻², consistent with literature values. The cathode was used to generate H₂O₂ at a rate of 420 ± 40 mg L⁻¹ h⁻¹ (25 mA cm⁻²), and nickel catalyst modification further increased the rate to 760 ± 60 mg L⁻¹ h⁻¹ (25 mA cm⁻²). Overall, the highly waterproof rolling phase inversion activated carbon air cathodes showed great promise for scaling up biotic and abiotic electrochemical systems for practical applications.

1. Introduction

Electrochemical technologies have been widely developed for domestic and industrial wastewater treatment applications such as microbial fuel cells (MFCs), electrochemical hydrogen peroxide production, and electrochemical advanced oxidation processes [1–3]. Many electrochemical systems have been based on the oxygen reduction reaction (ORR) at the cathode to take advantage of its favourable reduction potential, but most processes have required water aeration to provide adequate dissolved oxygen leading to undesirable high energy consumption [4–6]. Air cathodes have emerged more recently in these systems for catalyzing ORR owing to passive oxygen transfer from air and no need of aeration, which thereby reduced overall energy consumption in electrochemical processes [7,8]. Practical wastewater treatment often deals with tons of waste water per day, which requires hundreds of square meters of air cathodes in such electrochemical systems [9]. Also, most reported air cathodes have been fabricated by hand brushing or pasting in small scale, and therefore are not suitable for mass production [8,10–12]. Scalable fabrication of air cathodes is therefore

hindering the practical application of air cathode based electrochemical technologies.

A scalable air cathode should maintain low cost, relatively good performance and simple manufacture process. A typical air cathode consists of a three layer structure of current collector, catalyst layer and waterproof gas diffusion layer (GDL) [13]. Recent advances in inexpensive activated carbon (AC, ~ \$0.5 kg⁻¹) or modified carbon based catalysts [14,15], and the use of cheap metal current collectors (e.g. stainless steel mesh), have significantly reduced the overall material cost [16]. However, the development of a highly waterproof and air permeable GDL, and proper integration of the GDL into the cathode structure still remain challenging. A highly waterproof polytetrafluoroethylene (PTFE)/carbon black (CB) GDL (up to 3 m water head) was fabricated but it used high pressure rolling followed by sintering at 340 °C for 25 min, making it difficult and expensive to mass produce [1,17,18]. A commercial cathode made by VITO utilized pure PTFE as GDL and was reported to leak at relatively low water heads (<1 m) with obvious salt precipitation after long term operation, resulting in decreased cathode performance and potentially costly cathode

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replacement [12,19]. Another single-step phase inversion cathode was developed by hand pasting AC/CB/polyvinylidene fluoride (PVDF) mixture onto a stainless steel mesh current collector and then go through phase inversion process at room temperature. The phase inversion cathode was able to tolerate a water pressure head of 1.2 m (~12 kPa) without additional GDL, but hand pasting could result in defects at larger scales [8,16]. Therefore, scaling up the air cathodes requires both a defect-free GDL and a facile fabrication process.

Polyvinylidene fluoride (PVDF) membrane is a naturally hydrophobic and microporous membrane that has been widely used in membrane distillation [20], oil/water separation [21], and protein transfer [22]. PVDF membranes can be easily fabricated at meter scales without defect through non-solvent induced phase separation or thermally induced phase separation [23]. The hydrophobic microporous structure of a PVDF membrane provides abundant oxygen transfer channels and relatively high liquid entry pressures [24], which makes it suitable as a cathode GDL being both air permeable and watertight. But the integration of PVDF membrane tightly in cathode structure is difficult because the organic solvent (e.g. *N,N*-dimethylacetamide) used for binding carbon catalyst can readily dissolve the PVDF membrane [25,26]. Therefore, the PVDF membrane must be properly tailored to resist organic solvents in order to be utilized for scalable air cathode production.

An easily implementable rolling phase inversion process was developed in this work for scalable production of activated carbon air cathodes. The key innovation was to crosslink the PVDF membrane using ethylenediamine so that it could resist alteration in hydrophobicity and microporosity by the solvent. The crosslinked PVDF membrane was in one-step tightly integrated with activated carbon catalyst layer and stainless current collector through rolling phase inversion process at room temperature. The developed AC air cathodes were utilized in two model applications of electricity generation in a microbial fuel cell (MFC) and H₂O₂ production in an electrochemical cell.

2. Materials and methods

2.1. PVDF membrane crosslinking and cathode fabrication.

The PVDF membrane (0.45 μm, Merck Millipore, Germany) was rinsed with deionized (DI) water and dried at room temperature in a fume hood. The PVDF membrane was then crosslinked by immersing it in ethylenediamine (EDA) at 80 °C for 1 min [27]. After crosslinking, the PVDF membrane was washed with DI water at least three times to remove any residual reagent. Finally, the EDA crosslinked PVDF membrane was dried under ambient temperature prior to use. The crosslinked PVDF membrane was denoted as NH₂-PVDF.

The air cathode was fabricated by rolling the crosslinked PVDF membrane with carbon catalyst mixture and stainless steel mesh followed by a phase inversion process. A 10 % (w/v) PVDF solution was prepared by dissolving PVDF powder (~1,000,000, Bide Pharmatech, China) in *N,N*-dimethylacetamide (DMAc). The PVDF solution was vigorously stirred at 60 °C for over 6 h until the solution became clear. The carbon catalyst mixture was then prepared by mixing activated carbon (AC) (Acros, Belgium), carbon black (CB) (XFNANO, China) and PVDF solution (10 % w/v) at a mass ratio of AC:CB:PVDF = 30:3:10 as described previously [16]. The AC mixture was sandwiched between a stainless steel mesh (50 × 50, type 316L) and the NH₂-PVDF membrane. The sandwich cathode was then rolled using a Teflon roller to bind the NH₂-PVDF membrane with the carbon catalyst mixture and stainless steel mesh. Since the carbon catalyst mixture was relatively fluidic and sticky using PVDF as the binder, low pressure rolling was enough to spread out the carbon catalyst evenly and bind firmly with the NH₂-PVDF membrane and stainless steel mesh. The rolling thickness was controlled at 1.1 ± 0.1 mm on account of the thickness of NH₂-PVDF membrane and stainless steel mesh, resulting in a final carbon catalyst layer thickness of 0.6 ± 0.1 mm (~26.5 mg cm⁻² of activated carbon

and ~ 8.8 mg cm⁻² of binder). To induce the phase inversion process and extract the DMAc organic solvent, the roller pressed cathode was immersed in DI water at 25 °C for 15 min [16], and then air dried in a fume hood for over 8 h at room temperature before testing. A PVDF cathode was similarly fabricated using non-crosslinked PVDF membrane following the above procedures. As a comparison, a control AC cathode without PVDF membrane as GDL was fabricated as previously described [16].

2.2. Membrane characterization and cathode performance

Organic solvent resistance test was conducted to explore the stability of crosslinked PVDF membrane because the PVDF membrane would get in contact with DMAc during the rolling process. A droplet of 20 μL DMAc solvent was dropped on PVDF membranes and maintained for 20 s. The membranes were then washed in DI water for 5 min to remove any residual organic solvent. The membranes were then characterized with SEM for morphological change.

The liquid entry pressure (LEP) (in m of static water head) for membranes and cathodes were measured in a customized crossflow filtration cell as previously described [28]. The effective testing area was 8 cm² and DI water was used as the feed solution. The feed pressure in the chamber was gradually increased at an interval of 0.5 bar (~5.1 m water height) until the water penetrated the membranes or cathodes, and leaked into the effluent side. Each pressure was stabilized for 20 min for accuracy. The LEP was recorded as the transmembrane pressure prior to water penetration.

Cubic single chamber MFCs constructed from a Lexan block with 4 cm in length and 3 cm internal diameter were used to examine the cathode performance [29]. The MFC power curves were obtained in single chamber MFCs by sequentially decreasing the external resistance from 1000 through 500, 200, 100, 75, 50 to 20 Ω at 20 min interval (SI, section 1.5) [10]. The electro-production of H₂O₂ were performed in an electrochemical cell with two chambers (2 cm length, 3 cm diameter) separated by a cation exchange membrane (CMI-7000, Membrane International Inc., USA) [10]. Galvanostatic mode was applied with a DC power (DP305C, Mestek, Shenzhen, China) at different currents of 35, 70, 105, 140 and 175 mA as detailed in SI, section 1.6.

3. Results and discussion

3.1. Characteristics of cross-linked PVDF membrane

The crosslinking of PVDF membrane significantly enhanced the organic solvent resistance without alteration of membrane structure. The microporous structure was well maintained for crosslinked the NH₂-PVDF membrane after treating with DMAc (Fig. 1C and 1D), while the plain PVDF membrane showed obvious large pore defects (Fig. 1A, 1B and S1) due to solvation by a polar aprotic solvent such as DMAc [30]. The polymer chains of NH₂-PVDF were restrained by amine crosslinkage formed via dehydrofluorination and conjugate addition (nucleophilic attack), while plain PVDF chains were easily swelled by DMAc and dissolved (Fig. 1E and 1F) [31]. The nitrogen peak intensities of NH₂-PVDF membranes gradually increased with increasing amination time from 20 s to 120 s, demonstrating improved crosslinking (Fig. 1G). Decreasing peak intensities of fluorine were observed with prolonged amination time due to enhanced dehydrofluorination (Fig. 1H) [32]. While higher crosslinking degree was favored for better organic solvent resistance, the 120 s crosslinking duration decreased the membrane mechanical strength with folded cracks (Fig. S3J). Therefore, 60 s of amination was adopted for NH₂-PVDF membrane crosslinking with balanced organic solvent resistance and mechanical strength.

LEP is the minimum transmembrane pressure required for the feed solution to penetrate the large pore size [33]. A high LEP represents strong waterproof capability of air cathode to withstand the water pressure in scale-up applications. The plain PVDF membranes exhibited

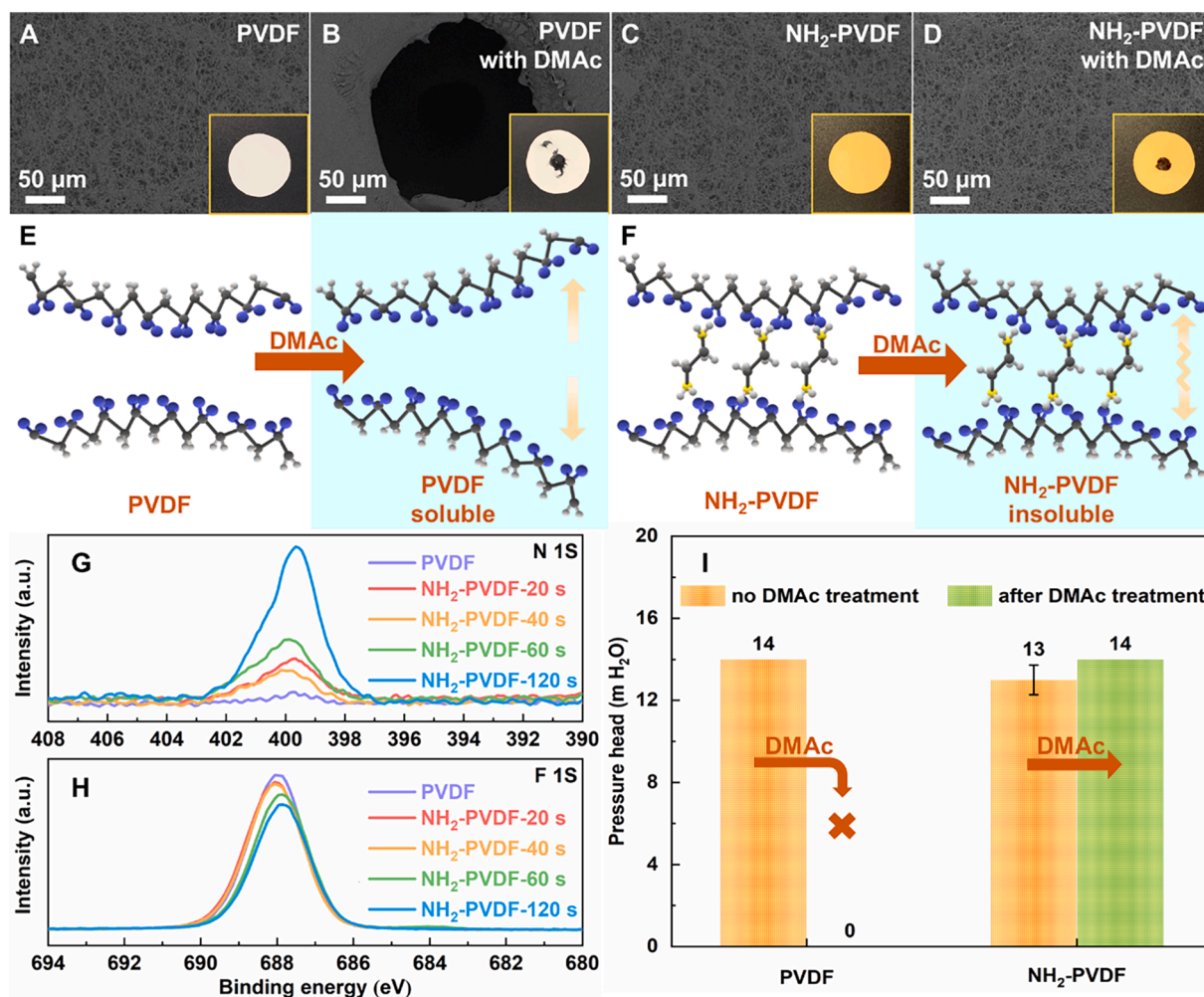


Fig. 1. SEM and photographic images of (A) PVDF membrane; (B) PVDF membrane treated with DMAC; (C) NH₂-PVDF membrane; (D) NH₂-PVDF membrane treated with DMAC. Schematic diagrams of the PVDF solubilization for (E) PVDF membrane and (F) NH₂-PVDF membrane before and after DMAC treatment. (G) XPS N 1s and (H) F 1s spectra of PVDF and NH₂-PVDF membranes aminated for 20, 40, 60, 120 s. (I) Water pressure head of PVDF and NH₂-PVDF membranes (60 s amination) before and after DMAC treatment.

an LEP of 14 ± 0 m water height, but sharply decreased to zero upon contacting the DMAC solvent (Fig. 1I). The NH₂-PVDF maintained a similar LEP of 13 ± 0.7 m H₂O height after DMAC treatment (Fig. 1I), which was by far the highest for GDLs and more than 5 times higher than that obtained in a previous study using PTFE/CB GDL sintered at 340 °C [7]. The LEP is proportional to the cosine of contact angle, the liquid surface tension and the geometric factor, and is inversely proportion to the largest pore size [34]. Thus, the low LEP of the plain PVDF membrane after DMAC treatment likely resulted from the formation of large holes due to solvation of the PVDF polymer (Fig. 1B). In contrast, the NH₂-PVDF membrane was still able to withstand a high water pressure of 14 ± 0 m due to its good organic solvent resistance and unchanged microporous morphology.

3.2. MFC performance with NH₂-PVDF cathode

In single chamber MFCs, a maximum power density of 1010 ± 40 mW m⁻² was obtained for NH₂-PVDF cathodes, which was the same as AC (1060 ± 10 mW m⁻²) and PVDF (1050 ± 10 mW m⁻²) cathodes (Fig. 2B). Polarization curves for AC and PVDF cathodes showed a steep drop at the current densities over 5 A m⁻² due to the power overshoot, which typically occurred at high current densities [35,36]. Similar cathode potentials and whole cell voltage generation over continuous operation were also obtained for three cathodes (Fig. S6), demonstrating

a minimal impact of additional NH₂-PVDF membrane on oxygen reduction reaction in the MFC. The power performance of NH₂-PVDF cathodes in MFCs were consistent with cathodes reported in other studies at the same testing conditions of feeding electrolyte, cathode size and reactor configuration [37]. Similar cathodic potentials between NH₂-PVDF, PVDF and AC cathodes were also observed at lower current densities of up to 8 A m⁻² in abiotic LSV test, which indicated oxygen transfer was not adversely impacted due to the extra PVDF layer on the NH₂-PVDF cathodes (Fig. S7). Besides, the long-term performance of air cathode was evaluated for an extended time of additional ~ 12 days (Fig. S8). The MFCs equipped with NH₂-PVDF cathodes showed stable voltage generations of ~ 500 mV during the whole operation period, demonstrating the stability of the fabricated NH₂-PVDF cathodes by roller phase inversion method. However, the long-term stability for applying the cathodes in real wastewater should also focus on preventing biofouling and potential salt precipitation [38,39], which could hinder proton transfer and block active sites of the carbon catalyst with decreased cathode performance. Overall, the additional waterproof layer of NH₂-PVDF membrane did not significantly increase the oxygen transfer resistance or impact the electrochemical performance of air cathodes in MFCs.

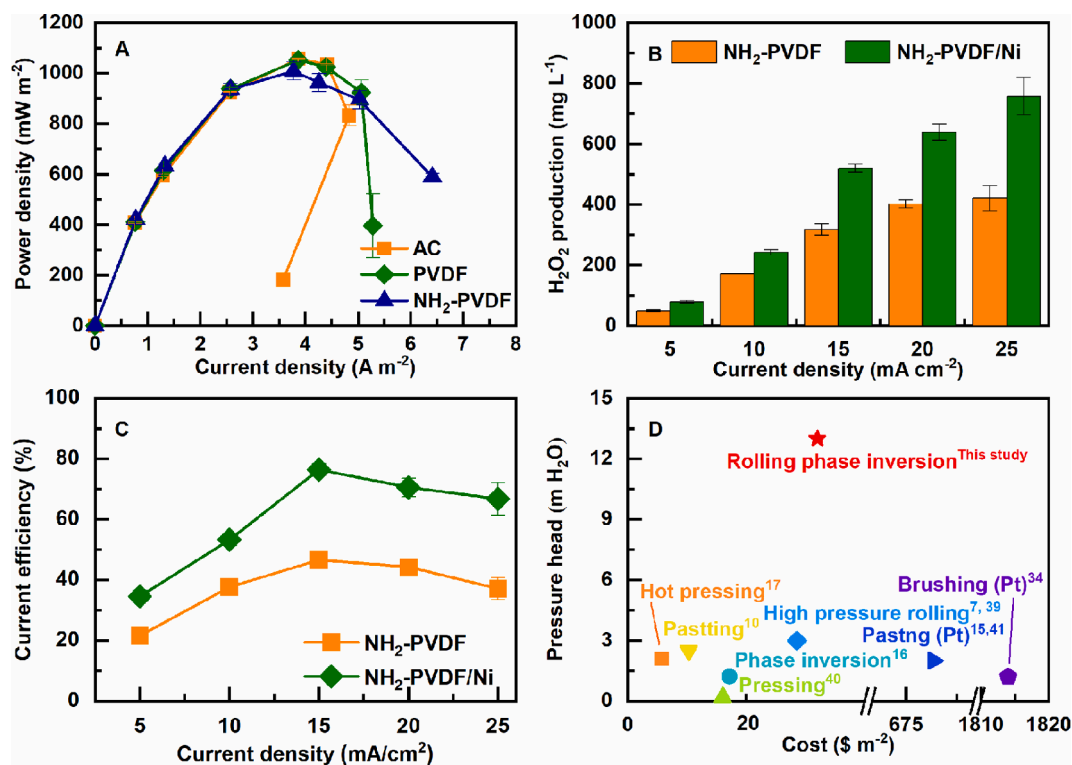


Fig. 2. (A) Power density curves for AC cathode, PVDF cathode and NH₂-PVDF cathode in MFC (50 mM PBS, 1000 Ω resistor, 1 g L⁻¹ CH₃COONa). (B) H₂O₂ production and (C) current efficiencies of NH₂-PVDF and NH₂-PVDF/Ni cathodes in 50 mM Na₂SO₄ solution with 1 h operation. (D) Water pressure resistance and cost analysis compared to previously reported air cathodes [7,10,15–17,37,46,49,50].

3.3. Electrochemical production of H₂O₂

H₂O₂ production using NH₂-PVDF cathodes reached 50 ± 3 mg L⁻¹ at 5 mA cm⁻² after 1 h operation, and further increased to 420 ± 40 mg L⁻¹ after 1 h at a current density of 25 mA cm⁻² (Fig. 2B). The production of H₂O₂ was mainly attributed to the CB catalyst because only 180 ± 5 mg L⁻¹ H₂O₂ was obtained at 25 mA cm⁻² with pure AC as the catalyst. The production of H₂O₂ was consistent with literature that CB is selective for the two-electron oxygen reduction reaction [40]. To further boost the H₂O₂ production, a nickel based layered double hydroxide (Ni-LDH) was synthesized according to literature and added into the NH₂-PVDF cathodes and produced 760 ± 60 mg L⁻¹ H₂O₂ at 25 mA cm⁻², which was ~ 81 % higher than that of NH₂-PVDF cathode (Fig. 2B) [41]. Both nickel modified or non-modified NH₂-PVDF cathodes produced higher H₂O₂ concentrations compared to previous reports at the same current density [8,42], demonstrating the performance feasibility of proposed rolling phase inversion cathode.

The current efficiency (CE) of NH₂-PVDF/Ni cathode was higher than that of NH₂-PVDF cathode. The highest CE of the NH₂-PVDF/Ni cathode was 76.5 % at 15 mA cm⁻², which was 1.6 times as much as that for the NH₂-PVDF cathode (46.6 %) (Fig. 2C). The CE increased at first for both the NH₂-PVDF cathodes with or without Ni modification, and then decreased with increasing current density, which was due to side reaction of hydrogen evolution. The surge of hydrogen would hinder the mass transfer of oxygen and electrolyte, limiting the oxygen reduction reaction [43].

3.4. Scalability and cost analysis

The scaling up of air cathodes has long been hindered by large area production of GDL as being both waterproof and air permeable. Here, the crosslinked NH₂-PVDF membrane as GDL can well maintain its microporous structure without defects, allowing air permeance and being highly waterproof (Fig. 1D and 1H). Owing to the strong organic

solvent resistance, the NH₂-PVDF membrane can be easily integrated into a low-pressure rolling phase inversion process to fabricate by far the largest single-piece air cathode of 1000 cm² with 40 cm in length and 25 cm in width in laboratory condition (Fig. S9). A previously reported brushed air cathode with AC/CB catalysts using PVDF as the binder was successfully scaled up to 707 cm², but it showed decreased electrochemical performance due to an uneven catalyst layer resulting from manual brushing [8,44]. Other reported cathodes were mostly much smaller (between 10 and 100 cm²), and fabricated through complicated procedures (e.g. high temperature) [10–12]. In general, the proposed low pressure rolling phase inversion method avoided complicated treatment procedures and the direct use of meter scale NH₂-PVDF membrane as GDL completely eliminated potential defects, which are critical for scaling up air cathodes.

The NH₂-PVDF rolling phase inversion cathodes obtained by far the highest water pressure resistance of ~ 13 m H₂O height, with an overall material cost of \$28 m⁻² (Fig. 2D). The main material cost was from the commercial PVDF membrane of ~ \$23 m⁻², and stainless steel mesh of \$4 m⁻² (Table S2). The cost of the catalyst layer made of AC (\$0.5 kg⁻¹), CB (\$2.5 kg⁻¹) and PVDF binder (\$10 kg⁻¹) was negligible. Although the cost of NH₂-PVDF cathode was slightly higher than pressed or rolled AC air cathodes [16], the cost of \$28 m⁻² was still much lower than anticipated \$110 m⁻² for mass manufacture of air cathodes as estimated in another study on scaling up microbial electrochemical technologies [9]. The long-term cathode cost could be further reduced by controlling biofouling and salt precipitation to extend the cathode lifetime. Moreover, the water pressure tolerance of ~ 13 m H₂O height was much higher compared to that of previously reported cathodes ranging from just 0.2 to 3 m [37,45], which fulfills the requirement for practical water or wastewater treatment typically dealing with tons of water daily [46]. Apart from reducing cost, the sustainability and environmental friendliness should also be considered. Thus, triethyl phosphate (TEP), an alternative green solvent for dissolving PVDF [47,48], could potentially be adopted in future studies and scale-up fabrication.

4. Conclusions

Mass manufacturing of AC air cathode at large scales is crucial for applying air cathode-based electrochemical technologies towards practical water/wastewater treatment. Herein, a low-pressure rolling phase inversion method was proposed for scaling up AC air cathodes with competing electrochemical performance as exemplified in MFCs and electro-H₂O₂ production. The use of crosslinked NH₂-PVDF membrane as GDL completely eliminated cathode defects and obtained the highest waterproof capability with marginally increased material cost. The facile and simple fabrication procedure of rolling phase inversion cathode without high temperature and pressure can greatly advance the scale-up studies of electrochemical water/wastewater treatment.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2022.140411>.

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