Short communication

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

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ARTICLE INFO

Keywords:
Air cathode
Scale-up
Rolling phase inversion
PVDF gas diffusion layer
Amination

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 (NH\textsubscript{2}-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 cm\textsuperscript{2} with a high pressure resistance of 13 ± 0.7 m H\textsubscript{2}O height (~137 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 NH\textsubscript{2}-PVDF cathodes produced a maximum power density of 1010 ± 40 mW m\textsuperscript{-2}, consistent with literature values. The cathode was used to generate H\textsubscript{2}O\textsubscript{2} at a rate of 420 ± 40 mg L\textsuperscript{-1} h\textsuperscript{-1} (25 mA cm\textsuperscript{-2}), and nickel catalyst modification further increased the rate to 760 ± 60 mg L\textsuperscript{-1} h\textsuperscript{-1} (25 mA cm\textsuperscript{-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\textsuperscript{-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...
Chemical Engineering Journal 454 (2023) 140411

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 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 dissolved (Fig. 1E and 1F) [31]. The nitrogen peak intensities of the crosslinked PVDF membrane significantly enhanced the organic solvent resistance without alteration of membrane structure. 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. S2). 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 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]. The developed AC air cathodes were utilized in two ethylenediamine so that it could resist alteration in hydrophobicity and stainless current collector through rolling phase inversion process at microporosity by the solvent. The crosslinked PVDF membrane was therefore, the PVDF membrane must be properly tailored to 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 at room temperature. The developed AC air cathodes were utilized in two model applications of electricity generation in a microbial fuel cell.
an LEP of 14 ± 0 m water height, but sharply decreased to zero upon contacting the DMAc solvent (Fig. 1 I). The NH$_2$-PVDF maintained a similar LEP of 13 ± 0.7 m H$_2$O height after DMAc treatment (Fig. 1 I), which was by far the highest for GDLs and more than 5 times higher than that obtained in a previous study using PTFE/CB GDLs 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 proportional 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. 1 B). In contrast, the NH$_2$-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 NH$_2$-PVDF cathode

In single chamber MFCs, a maximum power density of 1010 ± 40 mW m$^{-2}$ was obtained for NH$_2$-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 NH$_2$-PVDF membrane on oxygen reduction reaction in the MFC. The power performance of NH$_2$-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 NH$_2$-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 NH$_2$-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 NH$_2$-PVDF cathodes showed stable voltage generations of ~ 500 mV during the whole operation period, demonstrating the stability of the fabricated NH$_2$-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 NH$_2$-PVDF membrane did not significantly increase the oxygen transfer resistance or impact the electrochemical performance of air cathodes in MFCs.

Fig. 1. SEM and photographic images of (A) PVDF membrane; (B) PVDF membrane treated with DMAc; (C) NH$_2$-PVDF membrane; (D) NH$_2$-PVDF membrane treated with DMAc. Schematic diagrams of the PVDF solubilization for (E) PVDF membrane and (F) NH$_2$-PVDF membrane before and after DMAc treatment. (G) XPS N 1 s and (H) F 1 s spectra of PVDF and NH$_2$-PVDF membranes aminated for 20, 40, 60, 120 s. (I) Water pressure head of PVDF and NH$_2$-PVDF membranes (60 s amination) before and after DMAc treatment.
3.3. Electrochemical production of $\text{H}_2\text{O}_2$

$\text{H}_2\text{O}_2$ production using NH$_2$-PVDF cathodes reached $50 \pm 3$ mg L$^{-1}$ at 5 mA cm$^{-2}$ after 1 h operation, and further increased to $420 \pm 40$ mg L$^{-1}$ after 1 h at a current density of 25 mA cm$^{-2}$ (Fig. 2B). The production of $\text{H}_2\text{O}_2$ was mainly attributed to the CB catalyst because only $180 \pm 5$ mg L$^{-1}$. $\text{H}_2\text{O}_2$ was obtained at 25 mA cm$^{-2}$ with pure AC as the catalyst. The production of $\text{H}_2\text{O}_2$ was consistent with literature that CB is selective for the two-electron oxygen reduction reaction [40]. To further boost the $\text{H}_2\text{O}_2$ production, a nickel based layered double hydroxide (Ni-LDH) was synthesized according to literature and added into the NH$_2$-PVDF cathodes and produced $760 \pm 60$ mg L$^{-1}$ $\text{H}_2\text{O}_2$ at 25 mA cm$^{-2}$, which was ~81% higher than that of NiH$_2$-PVDF cathode (Fig. 2B) [41]. Both nickel modified or non-modified NH$_2$-PVDF cathodes produced higher $\text{H}_2\text{O}_2$ 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 NH$_2$-PVDF/Ni cathode was higher than that of NH$_2$-PVDF cathode. The highest CE of the NH$_2$-PVDF/Ni cathode was 76.5% at 15 mA cm$^{-2}$, which was 3.8 times as much as that for the NH$_2$-PVDF cathode (46.6%) (Fig. 2C). The CE increased at first for both the NH$_2$-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 NH$_2$-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 NH$_2$-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 cm$^2$ 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 cm$^2$, 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 cm$^2$), 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 NH$_2$-PVDF membrane as GDL completely eliminated potential defects, which are critical for scaling up air cathodes.

The NH$_2$-PVDF rolling phase inversion cathodes obtained by far the highest water pressure resistance of ~13 m H$_2$O 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 NH$_2$-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 H$_2$O 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 cathodes with competing electrochemical performance as exemplified in MFCs and electro-H₂O₂ production. The use of crosslinked NH₃-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.

Acknowledgments

This work was supported by the National Science Foundation of China under Grant No. 52100021.

Appendix A. Supplementary data

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

References


