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Emerging methanol-tolerant AlN nanowire oxygen reduction electrocatalyst for alkaline direct methanol fuel cell

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Replacing precious and nondurable Pt catalysts with cheap materials is a key issue for commercialization of fuel cells. In the case of oxygen reduction reaction (ORR) catalysts for direct methanol fuel cell (DMFC), the methanol tolerance is also an important concern. Here, we develop AlN nanowires with diameters of about 100–150 nm and the length up to 1 mm through crystal growth method. We find it is electrochemically stable in methanol-contained alkaline electrolyte. This novel material exhibits pronounced electrocatalytic activity with exchange current density of about 6.52×10^{-8} A/cm². The single cell assembled with AlN nanowire cathodic electrode achieves a power density of 18.9 mW cm⁻². After being maintained at 100 mA cm⁻² for 48 h, the AlN nanowire-based single cell keeps 92.1% of the initial performance, which is in comparison with 54.5% for that assembled with Pt/C cathode. This discovery reveals a new type of metal nitride ORR catalyst that can be cheaply produced from crystal growth method.

Direct methanol fuel cell (DMFC) is one of the most attractive power sources for portable and vehicular applications due to the simplicity of the system and the adaptability of the liquid fuel^{1,2}. At present, the commercialization of DMFCs is hindered by several issues, including crossover of methanol from anode to cathode^{3,4}, as well as the dependence on precious Pt catalyst for methanol oxidation and oxygen reduction reactions^{5,6}. Methanol transported through the membrane will be electrochemically oxidized at the cathode, thus reducing the cathodic reactant. And in intermediate reactions during this process, for instance the adsorption of carbon monoxide onto the catalyst surface, the cathode will also be poisoned, which further lowers its performance^{7–9}.

Thus, the methanol-tolerant oxygen reduction reaction (ORR) catalysts have attracted much attention in recent years. One of the effective approaches is the nanostructured Pt alloy since Pt is the most effective electrocatalyst for ORR reaction. Pt-Pd Alloy Nanoflowers¹⁰, Pt/CoSe₂ Nanobelt¹¹, core-Shell Pt decorated PdCo¹² and numbers of Pt alloy nanoparticles^{13–16} fall into this category. Although great advances have been achieved for the improvement of methanol tolerance, a high usage of Pt metal is still of great concern for further practical applications of DMFCs.

In recent years, some promising non-precious catalysts have been developed towards oxygen reduction reaction, including Co or Fe-based macrocyclic compounds¹⁷, transitional metal chalcogenides¹⁸, nitrogen-doped carbon nanotubes¹⁹, nitrogen-doped ordered mesoporous carbon²⁰, and even nitrogen-doped graphene^{21,22}. The transition metal nitride catalysts also displayed methanol-tolerance for ORR reactions. In comparison with a sharp ORR current decrease of ~80% for commercial Pt/C catalyst after the addition of a 3 M methanol at 90 s in the LSV test, it was reported that a sulfur-nitrogen Co-doped carbon foam catalyst has no noticeable decrease under the same test condition²³. The similar behavior was also found for sulfur-nitrogen Co-doped graphene oxide²⁴ and Co-doping carbon blacks with nitrogen- fluoride²⁵.

With the recent advancement in anion-exchange membrane materials, there has been a growing interest in alkaline direct methanol fuel cell. Compared with proton exchange membrane under acidic environment, there are several significant advantages including the improved kinetics for both anodic alcohol oxidation reactions and cathodic oxygen reduction reactions, as well as a wide range of stable catalyst materials in alkaline media^{26–28}.

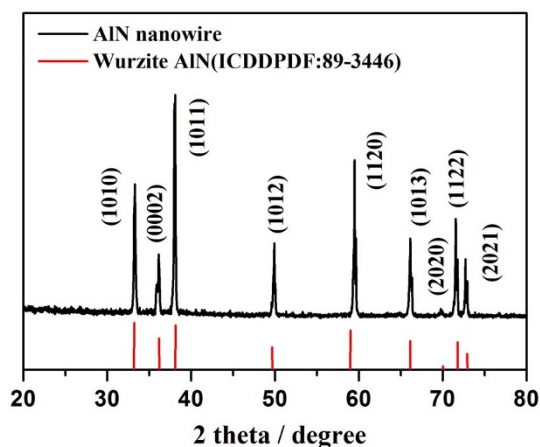


Figure 1 | XRD patterns of the AlN nanowire catalyst.

Many Pt-free catalysts exhibited excellent performance close to that of Pt in alkaline media, e.g., the maximum power density of alkaline direct methanol fuel cell assembled with fluorine-doped carbon black as the cathode achieved 14.56 mW cm^{-2} at 60°C , which is superior than a maxima of 9.44 mW cm^{-2} for commercial Pt/C²⁹. Graphitic carbon nitride exhibited comparable ORR activity, better durability and methanol tolerance ability in comparison to Pt/C³⁰.

Herein, we report an AlN nanowire with fine crystallization as oxygen reduction electrocatalyst in alkaline direct methanol fuel cell. Unlike the doped metal-N structure, the crystallized AlN is chemically stable in both acid and alkaline conditions, which should be helpful to improve the durability of fuel cells. The ORR activities were studied in an alkaline medium using cyclic voltammetry (CV) and rotating disk electrode (RDE) techniques. An alkaline direct methanol fuel cell test was constructed by using the so-formed materials as electrocatalyst in cathode. The performance of this single fuel cell demonstrated that the AlN nanowire catalyst is a promising methanol-tolerant candidate as oxygen reduction electrocatalyst for alkaline direct methanol fuel cell.

Results

The XRD pattern of the as-prepared sample (Figure 1) shows that the sample can be indexed as wurtzite AlN ($a = 3.113 \text{ \AA}$ and $c = 4.982 \text{ \AA}$), agreeing well with the calculated diffraction pattern (ICDD-PDF No. 25-1133). No impure peaks have been detected within the instrumental resolution, indicating that the sample is wurtzite AlN with high purity. Figure 2a gives an overall view of the sample collected from the crucible lid, revealing that there are large-scale ultralong AlN nanowires with high density. SEM image with higher magnifica-

tion (Figure 2b) indicates that the flexible nanowires are 100–150 nm in diameter and up to 1 mm in length with smooth surface and good toughness. The flexible structure and smooth surface of the ultralong nanowires are important for applications as catalyst in fuel cells. The typical TEM feature of a single AlN nanowire (Figure 2c) suggests a highly ordered and uninterrupted wire structure for the nanowires, where no segmentation or morphological imperfections, such as branching, are observed. High resolution TEM image (Figure 2d) indicates that an amorphous thin sheathed layer with thickness of 2–3 nm on the nanowire surface, and no defects like dislocations and stacking faults are found, indicating the high crystalline nature of the nanowires. The surface area of the AlN nanowire catalyst was determined by using the N_2 adsorption technique and the value is $43 \text{ m}^2/\text{g}$, which is close to the calculated value with diameter of 100 nm.

Figure 3 shows the polarization and power density curves obtained in an alkaline DMFC single cell with PtRu/C electrodes on the anode side and either AlN nanowire catalyst or Pt/C as the cathode electrodes at 60°C . Clearly, the initial cell performance and power density of the single cell equipped with Pt/C are superior to those recorded for AlN nanowire. The open circuit potential (OCP) for both single cells is of ca. 0.89 V. The maximum power densities are of ca. 30.5 and 18.9 mW cm^{-2} for single cells with Pt/C or AlN nanowire cathode electrodes, respectively. After being maintained at 100 mA cm^{-2} for 48 h, the situation changes drastically. As shown in Fig. 3b the OCP for both single cells decreases to around 0.8 V, while the maximum power densities decrease to 16.9 and 17.4 mW cm^{-2} for Pt/C-based single cell and AlN nanowire-based single cell, respectively. Remarkably, the effect of running time on performance of the single cell assembled with AlN nanowire catalyst is less pronounced compared to that on performance of the single cell using Pt/C catalyst. The origin for the superior methanol tolerance of AlN should be ascribed to the inertness of AlN toward methanol oxidation.

Discussion

Electrochemical property of the AlN nanowire catalyst was performed by using cyclic voltammetry (CV) in N_2 saturated 1 M KOH aqueous solution electrolyte with a scan rate of 50 mV s^{-1} (Figure 4). No significant oxidation or reduction current peaks are observed in the CV curve recorded from N_2 saturated solution, indicating that the novel catalyst is electrochemically stable over the entire potential range (-0.9 – $+0.2 \text{ V vs. MMO}$). These results differed from other reports on non-noble ORR catalysts such as Fe-N/C containing instable metal ions that present redox couples within the electrochemical windows¹⁸. Furthermore, no significant oxidation or reduction current peak is observed in the curves when methanol was presented in the solution, demonstrating that the AlN nanowire is also chemically stable in methanol.

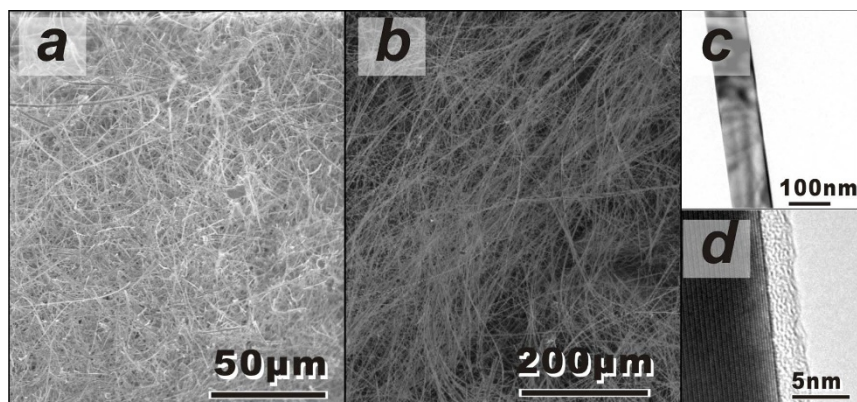


Figure 2 | SEM of the AlN nanowire grown on the substrate (a), and the collected AlN nanowire catalyst (b); (c) and (d) are TEM and high resolution TEM micrographs of the AlN nanowire, respectively.

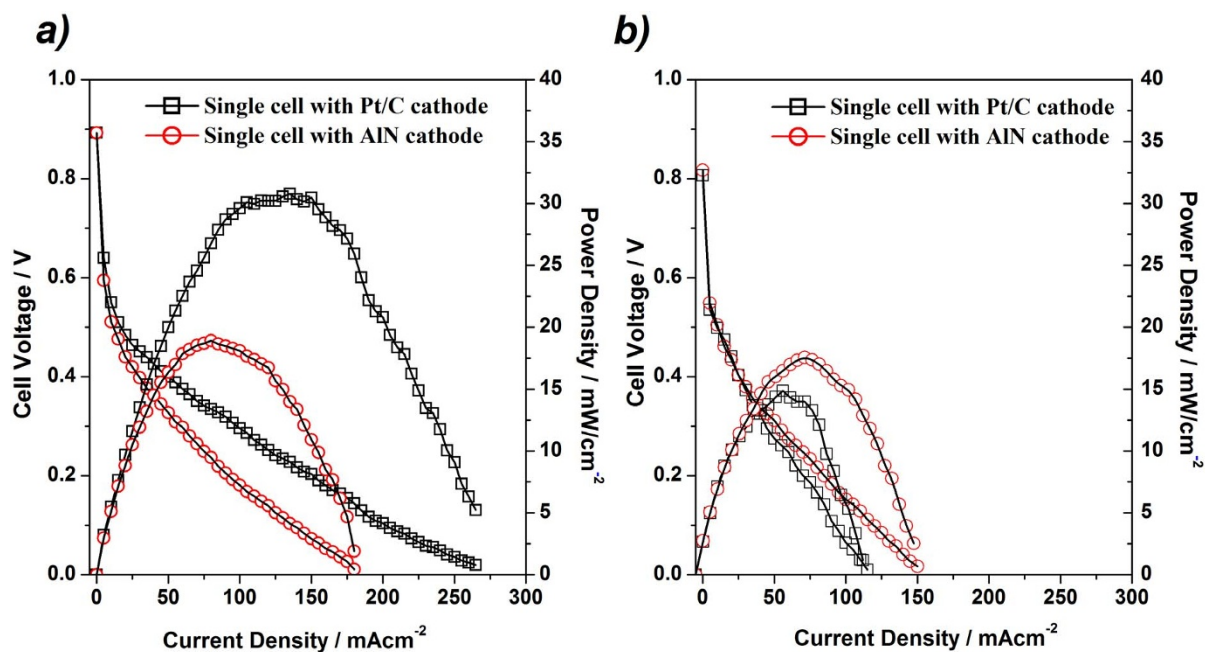


Figure 3 | (a) initial single cell performance, and (b) single cell performance after stabilized at 100 mA cm^{-2} for 48 h, of the single cell assembled with AlN cathode in comparison with Pt/C cathode.

To assess their ORR activity, the AlN nanowire coated electrodes were also tested in O_2 saturated KOH solution. As displayed in Figure 5, the reduction waves near -0.3 V vs. Hg/HgO indicate that the catalyst is active toward the ORR. The pronounced electrocatalytic activity is associated with an ORR onset potential at about -0.12 V vs. Hg/HgO. The cathodic current density achieved a value of -1.3 mA cm^{-2} at -0.28 V vs Hg/HgO. To examine the ORR kinetics and the corresponding kinetic parameters for the AlN nanowire catalyst, linear sweep voltammograms (LSVs) were recorded at various electrode rotation rates from 400 to 2000 rpm, in an O_2 saturated solution with a rotating disk electrode (RDE) (Figure 5a). The current at low-potential range shows a typical increase with rotation rate due to the attenuated diffusion layer. The onset potential of AlN nanowire is more negative than that of the commercial Pt/C catalyst, and it presents a slightly lower limiting current density than that of Pt/C, which consists with the results of single cell performance. However, for practical application in DMFC, the methanol crossover effect should also be considered. Thus, the current-time (*i-t*) chronoamperometric responses of Pt/C and AlN electrodes upon adding 3M methanol were recorded. (Figure. 5b) After the addition of methanol, the AlN electrode shows no noticeable change in its ORR current, indicating its superior methanol tolerance and high catalytic selectivity against methanol. While in contrast, an instantaneous current jump is observed for Pt/C electrode after the addition of methanol, which should be attributed to the initiation of methanol oxidation reaction (MOR). The different responses demonstrate the remarkably superior methanol tolerance of AlN nanowire to commercial Pt/C as the ORR catalyst.

By plotting applied electrode potential (*E*) as a function of $\log(i_d)$ (i_d is the disk current density), as shown in Figure 6, the Tafel slope and the intercept can be separately obtained. Thus, two important ORR kinetic parameters (the electron transfer coefficient, α , and the exchange current density, i^0) can be calculated. The exchange current density (i^0) calculated through a Tafel equation is about $6.52 \times 10^{-8} \text{ A/cm}^2$, close to the exchange current density obtained for the O_2 reduction on the Pt microelectrodes at acidic condition^{31,32}. The number of electrons transferred (*n*) is calculated to be ~ 2.45 at -0.1 – -0.2 V vs. Hg/HgO from the slopes of the Koutecky-Levich

plots¹⁹, suggesting that the ORR catalyzed by the AlN nanowires is a mixed process of 2- and 4-electron transfer.

In conclusion, the crystallized AlN nanowires are electrochemically stable in alkaline conditions with or without methanol. No significant oxidation or reduction current peak is observed in the CV curve recorded from N_2 saturated solution in the investigated potential range. Linear sweep voltammograms (LSVs) demonstrates that the AlN nanowire catalyst has a pronounced electrocatalytic activity with ORR onset potential at about -0.12 V vs. Hg/HgO and a high cathodic current density of -1.3 mA cm^{-2} at -0.28 V vs Hg/HgO. The exchange current density is about $6.52 \times 10^{-8} \text{ A/cm}^2$ and is independent on the methanol addition in the electrolyte. Single cell performance achieves 18.9 mW cm^{-2} for the DMFC with AlN nanowire cathode electrodes. After being maintained at 100 mA cm^{-2} for 48 h, the AlN nanowire-based cell keeps 92.1% of the initial performance, in comparison with 54.5% for the cell assembled with Pt/C cathode. The results demonstrated the AlN nanowire catalyst is a promising methanol-tolerant candidate as oxygen reduction electrocatalyst for alkaline direct methanol fuel cells.

Methods

Preparation of the AlN nanowire catalyst. AlN nanowire catalyst was conducted in a RF-heated furnace capable in the temperatures of 1700°C . TaC crucible with 30 mm in diameter and 50 mm in depth was used. AlN source materials sintered at 1500°C for 2 h served as charge. Fiber growth was carried out under a nitrogen (99.999%) pressure of 0.6 atm and a distance of 10 mm between the source and crucible lid. The estimated temperature gradient between the source and crucible lid was $3\text{--}7^\circ\text{C/mm}$. After growing for 2 hours, the AlN nanowire catalyst was collected from the crucible lid.

Structure analysis of the AlN nanowire catalyst. The morphology and microstructure of the collected products were examined by SEM (Filiphs, XL-30) and HRTEM (Philip CM-200). The fiber orientation was identified by XRD. Here, XRD data were collected on a MACM18XHF diffractometer with $\text{Cu K}\alpha$ radiation. The nitrogen adsorption and desorption isotherms at 77 K were collected by using a Micrometrics ASAP 2020 system. The samples were degassed overnight prior to the test. Brunauer–Emmett–Teller (BET) surface areas were estimated over a relative pressure (*P/P*₀) range from 0.05 to 0.30.

Electrochemical performance of the AlN nanowire catalyst. The electrocatalytic characterization for the ORR on the electrocatalysts was evaluated in a 1 M KOH aqueous solution with or without methanol at 30°C using the Autolab PGSTAT-30

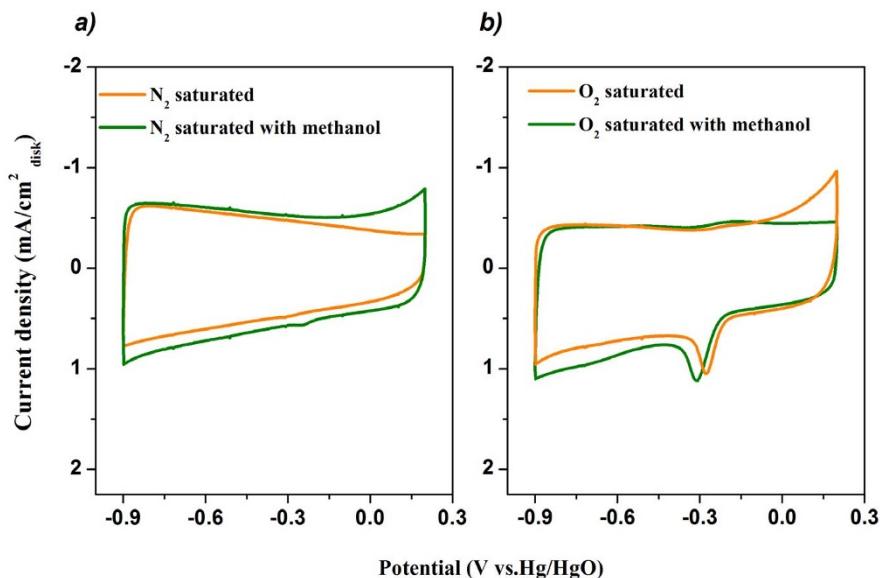


Figure 4 | Cyclic voltammetry of AlN nanowire catalyst as ORR catalysts in N_2 -saturated 1 M KOH (a) and O_2 -saturated 1 M KOH (b) with or without 2 M methanol.

electrochemical system. The electrochemical measurements were made in a classical three-electrode electrochemical cell with a Pt mesh counter electrode and Hg/HgO (MMO) reference electrode. To prepare the working electrode, 10 μ L of catalyst ink, consisting of 2 mg AlN nanowire catalyst per mL, was pipetted onto the surface of a GC disk electrode with a geometric area of 0.20 cm^2 . The catalyst loading was kept at 0.1 $mg\ cm^{-2}$. After the coating dried, 5 μ L of PBI solution (5wt% in Dimethylacetamide) was dropped onto the catalyst coating to form a catalyst layer.

Cyclic voltammograms and single-scan current-voltage curves were collected in the potential range of -0.9 – 0.2 V vs. MMO at 50 mV/s. To evaluate the alcohol crossover tolerance of the electrocatalysts, solutions of 1 M KOH with 2 M methanol were used as the electrolyte. Linear sweep voltammograms were conducted at 400, 800, 1200, 1600, and 2000 revolutions per minute (RPM) with a scan rate of 10 mV/s. The current–time (*i*–*t*) chronoamperometry was recorded for both Pt/C and AlN nanowire electrodes upon adding 3 M methanol at -0.4 V in O_2 -saturated 1 M KOH at a rotation rate of 1600 rpm.

Single cell performance of the AlN nanowire catalyst. KOH dope PBI film (100 μ m thick) were used as polymer electrolyte membrane as reported³³. Prior to fabricating electrodes, a homogeneous suspension composed of PTFE and carbon powder was sprayed onto the carbon paper (TGP-060, Toray Inc.) to form the gas diffusion layer with sublayer³⁴. Catalyst slurry was prepared prior to the MEA fabrication. A commercial PtRu/C (Johnson Matthey, 30 wt%, Pt:Ru 2:1) was used as anode whereas AlN nanowire catalyst or commercial Pt/C (Johnson Matthey, 40 wt%) was used at the cathode side. During the preparation, Pt-Ru/C (1 g), AlN nanowire (1 g)/ active carbon (0.3 g) or Pt/C(1 g) were mixed with 13 mL deionized water under vigorous stirring. Then 6.7 mL PBI solution (5wt% in Dimethylacetamide) was added to the mixture, followed by ultrasonic treatment for 30 min and a high-speed homogenizer for 1 h to form catalyst slurry. The catalyst slurry was applied to PTFE thin film by spraying. After dried at 60°C for 10 min followed with at 90°C in N_2 atmosphere for 3 min, the catalyst layer was then transferred onto the membrane at 125°C and 10 MPa by the decal method to form the catalyst-coated membrane

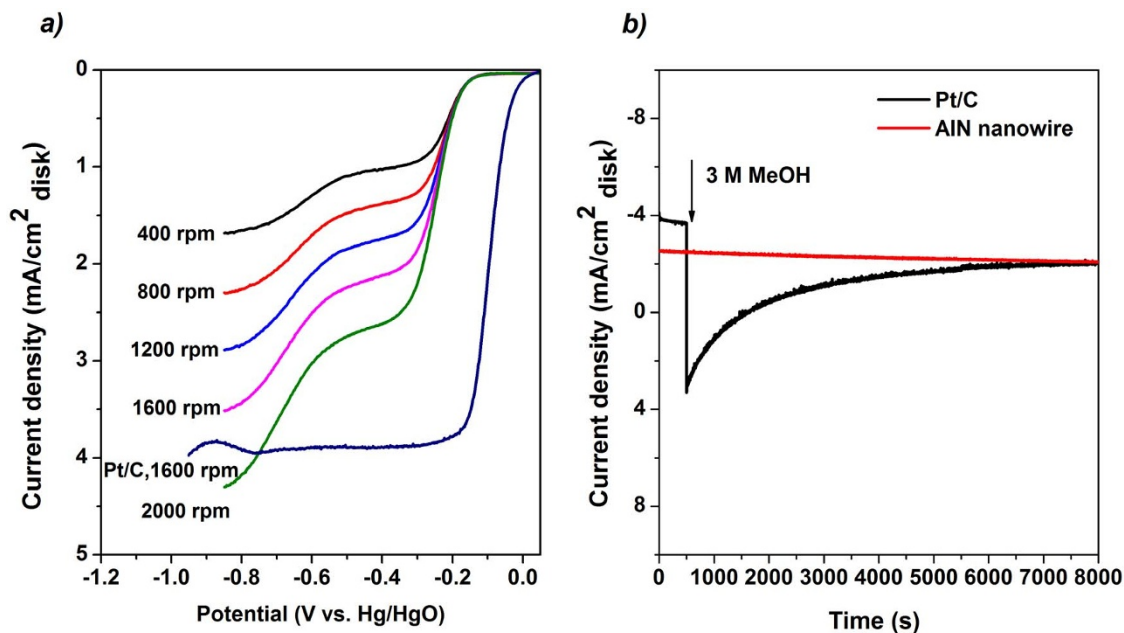


Figure 5 | (a) Linear sweep voltammograms of AlN nanowire and commercial Pt/C as ORR catalysts in O_2 saturated 1 M KOH. Scan rate: 10 $mV\ s^{-1}$. (b) Current–time (*i*–*t*) chronoamperometric response of Pt/C and AlN nanowire electrodes by adding 3 M methanol after 500 s at -0.4 V in O_2 -saturated 1 M KOH at a rotation rate of 1600 rpm.

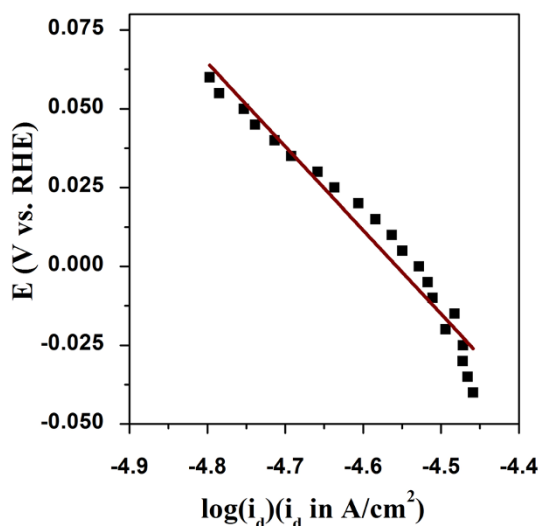


Figure 6 | Tafel plot of the AlN nanowire catalyst as ORR catalysts in O_2 -saturated 1 M KOH.

(CCM)³⁵. The gas diffusion layers were placed on the anode and cathode side of the CCM to form the MEA. The Pt or AlN loading for both the anode and cathode catalyst layer was controlled by weight and the value was 0.8 mg/cm².

Two flow-field plates made of high-density carbon with carved double-channel serpentine flow paths (1 mm wide and 1 mm deep) were fixed next to the MEA. Finally, the single fuel cell was assembled by two gold-plated copper end plates used as current collectors and assembled next to the flow-field plates. Fuel cells were tested at 60 °C under ambient pressure conditions using 2 M methanol in 1 M KOH aqueous solution as fuel into the anode and oxygen as oxidant into the cathode. The flow rates for methanol and oxygen were kept constant with values of 20 and 40 mL/min, respectively. The cell voltage (V) was obtained by varying the current at 5 mA intervals and equilibrated for 7 s between the intervals during the polarization curve measurement using an Autolab PGSTAT-30 electrochemical system.

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Author contributions

M.L., T.H.L. and W.J.W. conceived the idea, performed the experiments, analyzed and discussed data and wrote the paper; J.R.L. performed the characterization, revised the paper. J.W. and Y.G.W. contributed to the AlN synthesis, TEM and XRD experiments.

Additional information

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