Journal of Power Sources xxx (2017) 1–11

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Highly efficient transition metal and nitrogen co-doped carbide-derived carbon electrocatalysts for anion exchange membrane fuel cells

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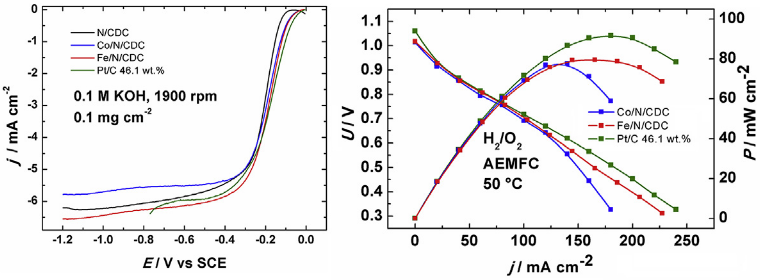
HIGHLIGHTS

- Highly porous M/N/CDC catalysts are synthesised from titanium carbide derived carbon.
- The overall pore size distribution stayed similar after metal and nitrogen doping.
- Both Co/N/CDC and Fe/N/CDC catalysts showed enhanced ORR activity in the RDE mode.
- MEAs based on M/N/CDC cathode catalysts are tested in AEMFC conditions.
- The peak power density reached was 80 mW cm^{-2}, only 10 mW cm^{-2} below that of Pt/C.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 June 2017
Received in revised form
10 August 2017
Accepted 13 August 2017
Available online xxx

Keywords:
Alkaline membrane fuel cell
Non-precious metal catalyst
Oxygen reduction
Electrocatalysis
Carbide-derived carbon

ABSTRACT

The search for an efficient electrocatalyst for oxygen reduction reaction (ORR) to replace platinum in fuel cell cathode materials is one of the hottest topics in electrocatalysis. Among the many non-noble metal catalysts, metal/nitrogen/carbon composites made by pyrolysis of cheap materials are the most promising with control over the porosity and final structure of the catalyst a crucial point. In this work we show a method of producing a highly active ORR catalyst in alkaline media with a controllable porous structure using titanium carbide derived carbon as a base structure and dicyandiamide along with $FeCl_3$ or $CoCl_2$ as the dopants. The resulting transition metal-nitrogen co-doped carbide derived carbon (M/N/CDC) catalyst is highly efficient for ORR electrocatalysis with the activity in 0.1 M KOH approaching that of commercial 46.1 wt.% Pt/C. The catalyst materials are also investigated by scanning electron microscopy, Raman spectroscopy and X-ray photoelectron spectroscopy to characterise the changes in morphology and composition causing the raise in electrochemical activity. MEA performance of M/N/CDC cathode materials in H_2/O_2 alkaline membrane fuel cell is tested with the highest power density reached being 80 mW cm^{-2} compared to 90 mW cm^{-2} for Pt/C.

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http://dx.doi.org/10.1016/j.jpowsour.2017.08.046
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Please cite this article in press as: S. Ratso, et al., Journal of Power Sources (2017), http://dx.doi.org/10.1016/j.jpowsour.2017.08.046

1. Introduction

A massive push towards limiting the impact of the hunger for energy of the modern way of life has yielded numerous research topics related to the conversion and storage of renewable energy in the recent years. The oxygen reduction reaction (ORR) plays part in a number of them, such as the electrification of automobiles via zinc-air batteries or fuel cells [1]. Fuel cells allow for the pollution-free conversion of chemical energy from hydrogen or other fuels into electrical energy which can then be used. To efficiently store the surplus energy available from renewable sources the loss during storage needs to be kept minimal and thus highly efficient platinum-based catalysts have mostly been used for oxygen reduction electrocatalysis in fuel cells to date [2]. However, the high price and scarcity of platinum mean that for the technology to be viable either the loadings have to be significantly reduced or platinum needs to be replaced with cheaper alternatives. Recently, high electrocatalytic activities for ORR have been achieved with doped carbon catalysts, which incorporate heteroatoms, such as nitrogen [3,4], cheaper and more abundant transition metals [2] or both [2,5–7]. In the former case, the electrocatalytic activity increase of carbon for ORR is related to the electron-donor abilities of the nitrogen atom doped into a carbon lattice [8,9] and it has recently been found via a rigorous study of numerous catalysts in acid media that pyrrolic nitrogen, where the nitrogen is in a five-member carbon cycle, catalyses the first step of oxygen reduction to hydrogen peroxide, which is then further reduced to water by pyridinic nitrogen, a moiety where the nitrogen is part of a six-member carbon ring [10]. As the stability of the intermediate HO_2^- adsorbate is higher in alkaline media compared to the equivalent H_2O_2 in acidic media, however, the mechanism is likely to be even more complex in alkaline conditions and needs further research. Unfortunately there is yet no way to synthesise a catalyst containing only a single type of nitrogen in a carbon lattice and the studies with catalysts containing high concentrations of either one or the other have reached differing conclusions [11–14]. In the case of both nitrogen and transition metal incorporating catalysts the increase in the ORR activity when introducing heteroatoms to the carbon lattice is ascribed to either $M\text{-}N_x$ active sites consisting of a metal atom coordinated to surrounding nitrogen moieties (usually four) [15–17] or nitrogen doped graphitic carbon on underlying metal/metal carbides [18,19]. In the former case O_2 undergoes a complete four-electron transfer in alkaline media on the $M\text{-}N_4$ site doped into the carbon lattice [20], while in the latter case the oxygen reduction takes place on the N-doped carbon via a $2e^-+2e^-$ pathway where the intermediate HO_2^- is stabilised by the subsurface metal/metal carbides [18].

Other than the active sites themselves, the disorder and the porosity of the carbon incorporating the active sites have been found to be among crucial descriptors for rational design of non-noble metal ORR electrocatalysts. The disorder of the carbon material notes a lower degree of π-electron delocalisation and higher electron-withdrawing capability, which enhances the activity of $M\text{-}N_x$ active sites by shifting the redox potential of the central metal ion anodically [20]. The active sites themselves have long been thought to reside in micropores with a width up to 22 Å [21,22], but recent results reveal that while a high microporosity might lead to a high initial activity in proton exchange membrane fuel cells (PEMFC), the pore flooding due to H_2O formation will lead to a rapid loss of catalytic activity [23,24]. This is easily avoided by using an anion exchange membrane fuel cell (AEMFC), where the water is formed on the anode. The ORR activity of non-noble metal catalysts in alkaline media is also generally higher than in acidic media [25]. The alkaline environment presents its own challenges due to the insufficient ion conductivity of currently commercially available membranes and sluggish anode kinetics [25–27], but the current catalytic activity of non-noble metal catalysts in AEMFC is also lacking [28]. A frequently used anion exchange membrane is Tokuyama's A201 along with the AS-4 ionomer also produced by the same company. Various results have been obtained with non-noble metal materials as well with Pt-based catalysts on the cathode, with the highest power density at 387 mW cm^{-2} using Pt/C and 248 mW cm^{-2} using a cobalt oxide-decorated N-doped graphene catalyst [29] in a highly optimised system with a high cathode and anode catalyst loading, which is known to affect activity in AEMFCs as the anode reaction is also somewhat sluggish [28]. Mostly peak power densities using Tokuyama A201 as the AEM fall between 60 and 120 mW cm^{-2} depending on the optimisation of the system and preparation procedures, with no consensus yet reached as to the optimal conditions for ion exchange of the membrane to the OH^- form, ionomer content, humidifying and activation procedures [30–36]. These factors and especially the method used for covering either the anion-exchange membrane or gas diffusion layer with the catalyst along with hot-pressing conditions are obviously crucial for reaching high ORR activities and a standard procedure would simplify comparing reported activities in the literature. Recently, very high peak power densities have been reached by using PtRu/C anode catalysts [27] and novel anion exchange membranes [37], both of which could bring important improvements to the AEMFC performance for non-noble metal catalyst cathode layers.

Taking the aforementioned notions on catalyst activity into account, a good ORR catalyst should thus have a high concentration of active sites and a high surface area coupled with a high microporosity and also be highly disordered. Numerous methods have been developed to synthesise such catalysts: the metal-organic framework derived-method [15,16], the sacrificial substrate method [17] or pyrolysis of metal salts in the presence of a polymer [38] or simple organic molecules [39–41] containing nitrogen and a carbon support. For the carbon support, traditional Pt catalyst support materials such as Ketjenblack and Vulcan carbon have been used, yet substituting these for a carbon nanomaterial that has more of the desired properties in the first place has been shown to be a valid strategy for retaining the structure in the final catalyst [42,43]. We thereby show a method for producing a highly active metal and nitrogen doped AEMFC catalyst from titanium carbide derived carbon, a highly disordered carbon material with a very large specific surface area and degree of microporosity. Scanning electron microscopy, X-ray photoelectron spectroscopy and the BET method are used for characterisation of the materials. Their electrocatalytic activity towards the ORR is studied in alkaline media using a rotating disk electrode.

2. Experimental

2.1. Synthetic procedure for M/N/CDC

Carbide-derived carbon (CDC) powders produced from titanium carbide using a patented chlorination procedure [44] were purchased from Skeleton Technologies OÜ (Estonia). 200 mg of the as-received material was weighed into a ball-mill with 10 wt.% of polyvinylpyrrolidone (PVP) and ethanol added to the mixture to achieve a motor-oil like viscosity and then ball-milled for 1 h at 800 rpm using 50 ZrO_2 balls (5 mm in diameter) to reduce the grain size of the CDCs. After ball-milling the mixture was separated from the balls, dried and then dispersed in isopropanol into which dicyandiamide (DCDA) 20 times the weight of the CDC material was added along with 2.5 wt.% of iron or 5.0 wt.% of cobalt in the form of chlorides. This suspension was then sonicated for 2 h before drying in vacuum. The dried material was pyrolysed in a quartz tube at

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