Cobalt- and iron-containing nitrogen-doped carbon aerogels as non-precious metal catalysts for electrochemical reduction of oxygen

Ave Sarapuu a,*, Lars Samolberg a, Kristiina Kreek b, Mihkel Koel b, Leonard Matisen c, Kaido Tammeveski a

a Institute of Chemistry, University of Tartu, Ravila 14A, 50411 Tartu, Estonia
b Institute of Chemistry, Tallinn University of Technology, Akadeemia tee 15, 12618 Tallinn, Estonia
c Institute of Physics, University of Tartu, Ravila 14C, 50411 Tartu, Estonia

1. Introduction

In recent years, development of non-precious metal catalysts (NPMCs) for oxygen reduction reaction (ORR) has attracted a great deal of attention, as these are good candidates to substitute expensive Pt-based catalysts in the fuel cell cathodes [1–4]. These materials are typically derived from various transition metal and nitrogen compounds on carbon supports by means of heat treatment in inert atmosphere. A large variety of precursors and synthetic procedures has been explored in order to increase the activity and stability of these catalysts. However, the exact mechanism of O2 reduction on these materials, the precise nature of active sites and the role of transition metals is still under debate [1–4]. Although rather promising results have been obtained using the metal-free nitrogen-doped carbon catalysts [5–13], it has been suggested that this may arise from metal impurities present in the starting materials, for instance, carbon nanotubes [14]. Considerably more active NPMCs have been synthesised in the presence of transition metals [15–42]. In alkaline solution, the activity of these novel catalyst materials can even surpass that of the commercial Pt catalysts [16,19,20,34–36]. It has recently been suggested that at high pH, the reduction of O2 proceeds primarily on Fe–nitrogen coordinated sites (Fe2+–N4) embedded into π-conjugated carbon basal plane [43,44].

The NPMCs can be synthesised on the basis of different carbon nanomaterials, like carbon nanotubes, carbon black, graphene, porous carbon structures etc. [4]. A promising class of materials are carbon aerogels (CAs) due to their unique properties, such as low mass density, continuous and tuneable porosity, high surface area, good conductivity and chemical stability [45]. The most traditional method for synthesising carbon aerogels is using templates (e.g. silica, zeolites or some polymers) that can be removed during or after carbonisation of organic precursors, thereby achieving highly porous nanocarbons with determined pore size [29,46,47]. Another common technique is carbonisation of solid organic aerogels, which are usually obtained by sol–gel polycondensation of various organic monomers (e.g. resorcinol, phenol, formaldehyde etc.) [46,47]. The pore size and structure of the resulting carbon aerogels can be controlled through synthesis conditions, such as the composition and drying method of the organic gel, temperature and duration of the pyrolysis etc. [46,47].

Another new and sustainable approach is to use various biomass-derived porous organic materials as precursors of carbon aerogels [46,47].

Thanks to their affordable price and unique chemical and physical properties, CAs have numerous potential applications. These materials may be used as adsorbents, advanced catalyst supports, electrode materials for supercapacitors, rechargeable batteries and fuel cells etc. [45]. To be used as cathode catalysts for low-
temperature fuel cells, high activity towards the ORR is necessary, which can be achieved through selection of the suitable precursors for the preparation of organic aerogels and/or further modification of the aerogel surface. Also the favourable physical properties, such as high electrical conductivity, high surface area and suitable pore structure contribute to the performance of the catalyst [45]. For the fuel cells, optimising the structure of the noble metal catalysts is still actual and there are several studies of ORR on Pt nanoparticles supported on carbon aerogels [48–52]. However, most of the research efforts are nowadays directed to the development of NPMCs, where carbon aerogel-based catalysts have also displayed promising electrocatalytic properties. In some reports, N-doped [53,54] and N- and S-dual-doped [55] carbon aerogels prepared in the absence of metals have been employed as ORR catalysts. These materials have been prepared from sustainable precursors (glucose [53–55], ovalbumin [55], glucosamine [54] and phenolic compounds [54]) by hydrothermal carbonisation and it has been shown that N-doping increases their electrocatalytic activity. However, as compared to Pt-based catalysts, the activity of these materials for ORR was still rather low [53–55]. Similarly to the other carbon materials, carbon aerogels or xerogels with considerably higher activity towards the ORR can be synthesised in the presence of transition metals (usually Co or Fe) during the carbonisation step [56–62]. For instance, the organic xerogels have been prepared by sol–gel polymerisation of resorcinol with formaldehyde in NH3 atmosphere by heating at 100 °C/min to 800 °C, but somewhat lower in acidic solution [56]. Rather similar results in acid media were also observed for the xerogels prepared using melamine in the synthesis instead of resorcinol [58]. For carbon aerogels prepared from melamine, formaldehyde and Fe or Co salts, the activity in acid solution was rather similar for Fe- and Co-containing catalysts and both showed promising performance in direct methanol fuel cell [59]. It has also been shown that varying the melamine/resorcinol ratio in the synthesis of aerogels enables one to adjust the microstructure of the materials [60]. Highly active porous carbon catalysts for ORR have been synthesised by pyrolysis of metal salts and poly(ethyleneimine) [24], 4-aminoantipyrine [25–28] or cyanamide [29] as precursors, while using the silica template as sacrificial support enabled to achieve a determined pore structure.

In the present work, metal-containing nitrogen-doped carbon aerogels have been prepared and their electrocatalytic activity towards the ORR in alkaline solution has been evaluated. The activity and stability of Co- and Fe-containing electrocatalysts has been compared.

2. Experimental

2.1. Preparation and characterisation of carbon aerogels

The preparation of metal-doped carbon aerogels is based on the ion-exchange method [63,64]. In a typical experiment melamine (11.41 g, 0.09 mol) and 2,6-di-hydroxy-4-methylbenzoic acid, dHMBA (5.066 g, 0.03 mol) were added to distilled water (100.0 g, 5.555 mol). Sodium carbonate (1.598 g, 0.015 mol) was added and the solution stirred to obtain the sodium salt of dHMBA. Formaldehyde (11.85 g, 0.395 mol) was added to the solution and then finally the catalyst, sodium carbonate (0.1278 g, 0.0012 mol). The solution was heated at 70 °C for 30 min to dissolve melamine. After that the solution was poured into glass test tubes and allowed to gel and cure for three days at 85 °C. 2,6-dihydroxy-4-methylbenzoic acid, with a purity of >99% was donated by Carboshale OU, Estonia. Melamine, with a purity of >99%, was purchased from Aldrich. Anhydrous sodium carbonate with purity of 99.8% was purchased from Riedel-de Haen, Germany. Formaldehyde (37% w/w solution in water) was purchased from Sigma–Aldrich.

To obtain Co2+- or Fe3+-containing gels, the hydrogels were soaked in 0.1 M solution of cobalt or iron nitrate for 3 days (the solution was changed after every 24 h), after which the sodium ions in the ion-exchange moiety (carboxylic group) are exchanged for Co2+ or Fe3+ ions, respectively. Cobalt(II) nitrate nonhydrate (>98%) and iron(III) nitrate (>98%) were purchased from Sigma–Aldrich.

In order to use supercritical CO2 drying for aerogel preparation, solvent exchange for acetone was carried out by changing the solution after every 24 h, starting with 25:75 acetone and water mixture and proceeding with 50:50, 75:25 and finally 100% acetone for two days. The supercritical extraction system with a double clamp autoclave, 100 mL in volume, was constructed by NWA Analytische Meßgeräte GmbH, Germany. CO2 (99.8%) was obtained from AGA, Estonia. A more detailed description of the method used for supercritical drying has been published elsewhere [65].

Metal-doped carbon aerogels were prepared by pyrolysis in N2 atmosphere by heating at 10 °C/min to 800 °C and keeping there for 1 h. The pyrolysis oven type MTF 12/38/400 with a maximum temperature of 1200 °C was purchased from Carbolite, England. Carbon aerogels containing Co and Fe are denoted as Co-NCA and Fe-NCA, respectively. For comparison, carbon aerogel was prepared from the organic gel not subjected to the ion exchange treatment and this is denoted as NCA.

The X-ray diffraction (XRD) pattern was recorded with a Rigaku Ultima IV diffractometer by using a DtexUltra line detector. Cu Kα radiation was used with a Ni filter for removing Kβ radiation. The recorded diffractograms were analysed by Rigaku PDXL software. Scanning electron microscopy (SEM) images were taken using ZEISS FEG-SEM ULTRA 55 microscope.

X-ray photoelectron spectroscopy (XPS) was used to analyse the surface composition of carbon aerogels. The monolithic carbon aerogels were ball-milled to fine powder and glassy carbon plates were repeatedly coated with the suspension of catalyst powder in 2-propanol (4 mg ml−1) and dried at 70 °C. The XPS measurements were carried out with a SCIENTA SES-100 spectrometer using an unmonochromated Al Kα X-ray source (incident energy = 1486.6 eV), a take-off angle of 90° and a source power of 300 W. The pressure in the analysis chamber was below 10−9 Torr. Raw data was processed using CasaXPS software [66], data processing involved removal of k-α and k-β satellites, removal of background, and fitting of components. Background removal was done using Tougaard background, for fitting components Gauss–Lorentz hybrid function was used (GL 30, Gauss 70%, Lorenz 30%) for best fit.

Elemental analyses were performed by Spectra AA 220F flame atomic absorption spectrometer (Varian, USA) and vario MICRO cube (Elementar, Germany).

2.2. Electrode preparation and electrochemical measurements

For the rotating disk electrode (RDE) experiments glassy carbon (GC) disks (GC20-SS, Tokai Carbon) with the geometric area (A) of 0.2 cm2 were used as electrode substrates. The rotating ring-disk electrode (RRDE) experiments were carried out on a GC disk-Au ring electrode (Pine Research Instrumentation, A = 0.164 cm2, collection efficiency N = 0.22). The electrodes were polished to a mirror finish with 1 and 0.3 μm alumina slurries (Buehler). To remove the alumina residues, the electrodes were sonicated in Milli-Q water for 5 min. The carbon aerogels were ball-milled to fine powder and the catalyst ink was prepared by mixing 4 mg of the catalyst, 40 μl of Nafion® solution (5 wt% solution in lower alcohols,
Aldrich) and 960 μl of 2-propanol. For the 20 wt% Pt catalyst supported on Vulcan XC-72 carbon (E-TEK), the same procedure was used.

The ink was ultrasonicated for at least 40 min and a calculated amount was applied onto the GC electrode surface to obtain the desired catalyst loading. The catalyst-coated electrodes were dried in an oven at 65 °C for at least 15 min before measurements.

The oxygen reduction measurements were performed using an Autolab potentiostat/galvanostat PGSTAT30 (Eco Chemie B.V., The Netherlands) and the General Purpose Electrochemical System (GPES) software. For RDE experiments, an EDI101 rotator and a CTV101 speed control unit (Radiometer) were employed. For RRDE testing of catalyst material a Pine Research Instrumentation AFMSRX rotator and MSRX speed controlled were used. Experiments were conducted in a glass cell at room temperature (23 ± 1 °C), a Pt wire served as the counter electrode and a saturated calomel electrode (SCE) was used as a reference; all the potentials are referred to this electrode. Electrochemical experiments were carried out in 0.1 M KOH, saturated with Ar (99.999%, AGA) or O₂ (99.999%, AGA). Electrolyte solution was prepared from KOH pellets (p.a. quality, Merck). A continuous flow of gases was maintained over the solution during the electrochemical measurements. The RDE polarisation curves were obtained by scanning the potential from 0 V to –1.2 V at the scan rate of 10 mV s⁻¹ and various electrode rotation rates (ω) between 360 and 3100 rpm. For the data presentation and analysis, the background current registered in O₂-free solution was subtracted from the experimental current and current densities are calculated per geometric area of the electrode (A).

3. Results and discussion

3.1. Characterisation of catalyst materials

The surface morphology of CAs was evaluated using SEM (Fig. 1). The CAs have grainy structure and open pores are not visible in the materials. This morphology is similar to a melamine–formaldehyde resin [67]. Melamine CAs differ from typical resorcinol/formaldehyde aerogels by having a structure where separate spheres composing the carbon network are less distinguished [68]. The distribution of Co species in Co-NCA sample was rather homogeneous, as confirmed by backscattered electron (BSE) imaging (Fig. 1b). Lighter spots which could be attributed to areas composed of heavier atoms (Co nanoparticles) were not visible. However, for Fe-NCA the BSE image is evenly dotted with light spots (Fig. 1d).

The crystallographic nature of the metal-containing carbon aerogels was elucidated by XRD technique. Only one small peak was detected on both diffractograms, belonging to Co and Fe, respectively. Crystalline structures of metal oxides or nitrides were not observed unlike in previous cases [57,58]. The broad peak at 20–25° is assigned to the graphite (002) planes and indicates that the carbon structure is rather disordered. For previously prepared Co- and N-doped resorcinol/formaldehyde aerogels, peaks corresponding to graphitic structures were more pronounced [57,58]. The high content of melamine and therefore lower content of the resorcinol derivate and carbon in our materials probably inhibits the formation of graphitic structures and crystalline metal species.

The metal content of the catalysts determined by atomic absorption spectrometry (AAS) was 3.0 wt% and 5.2 wt% for Co-NCA and Fe-NCA, respectively. The nitrogen content in the Co-NCA, Fe-NCA and NCA was 17 wt%, 7.6 wt% and 21 wt%, respectively, higher than usually observed for N-doped carbon aerogels [54,58]. Decrease in the nitrogen content of NPMCs with increasing the loading of the metal precursors has been previously observed [22]. However, lower total nitrogen content does not necessarily cause lower ORR activity of the catalyst, as only the nitrogen centres of certain type are believed to be involved in the ORR electrocatalysis [3].

In order to determine the chemical environment of nitrogen atoms, the N1s peaks of high-resolution XPS spectra were deconvoluted to up to six symmetrical peaks (Fig. 3). For all catalyst  

Fig. 1. SEM images of Co-NCA (a and b) and Fe-NCA (c and d). (b) and (d) represent the backscattered electron images.
materials, main part of nitrogen on the surface was pyridinic (N1, 398.2 eV) [54] and pyrrolic (N3, 400.4 eV) [54], which is typical for the N-doped carbon catalysts. Pyridinic nitrogen is considered to be the main site for binding the transition metal and one of the most active centres for oxygen electroreduction [3]. Peak N2 (399.2 eV) between pyridinic and pyrrolic N can be attributed to amine [22,54,69,70], nitrile [16,20,70–74] or metal-coordinated N (399.2 eV) [54]. Small peak N6 can only be detected for the metal-free catalyst and has been related to chemisorbed nitrogen oxides [79].

3.2. Oxygen reduction

The electrocatalytic activity of carbon aerogels was evaluated by the RDE method. Fig. 4 presents sets of RDE voltammery curves in 0.1 M KOH for Co-NCA and Fe-NCA catalysts. It can be seen that the activity of the catalysts for oxygen reduction is very high, the onset potential of the ORR for Co-NCA is approximately –0.1 V and the half-wave potential (E_{1/2}) about –0.21 V. The current plateau is slightly inclined, which may be related to the porosity of the coating that causes the potential-dependent change of the O2 penetration depth inside the catalyst layer, or by inhomogeneous distribution of active sites on the electrode [80].

The RDE data were analysed using the Koutecky–Levich (K–L) equation [81]:

$$\frac{1}{I} = \frac{1}{J_k} + \frac{1}{J_d} = \frac{1}{nFkC_{O_2}} + \frac{1}{0.62nFD_0^{1/2} \nu^{-1/2} \sigma_b \sqrt{D}}$$

where j is the measured current density, j_k and j_d are kinetic and diffusion-limited current densities, respectively, n is the number of electrons transferred per O2 molecule, k is the rate constant for O2 reduction, F is the Faraday constant (96,485 C mol\(^{-1}\)), \(\omega\) is the electrode rotation rate (rad s\(^{-1}\)), \(C_{O_2}\) is the concentration of oxygen in the bulk (1.2 \times 10^{-6} mol cm\(^{-3}\)) [82], \(D_{O_2}\) is the diffusion coefficient of oxygen (1.9 \times 10^{-5} cm\(^2\) s\(^{-1}\)) [82] and \(\nu\) is the kinematic viscosity of the solution (0.01 cm\(^2\) s\(^{-1}\)) [83]. From the results of the K–L analysis, the number of electrons transferred per O2 molecule (n) was calculated at various potentials (Fig. 5). At high negative potentials (E < –0.9 V), the value of n was very close to 4, indicating that the reaction yields only water, but at more positive potentials n decreased until about n = 3.7 for Co-NCA and n = 3.2 for Fe-NCA, showing that the production of peroxide increases.

The rotating ring-disk electrode (RRDE) method was used for the determination of peroxide yield in ORR on Co-NCA and Fe-NCA catalysts (Fig. 6). The percentage of peroxide formation was calculated from [84]:

$$\phi = \frac{200I_{RHE}}{I_0 + I_{RHE}/N}$$

where \(I_{RHE}\) is ring current, \(I_0\) is disk current and N is the collection efficiency of the ring (N = 0.22). For Co-NCA, the value of \(\phi\) was about 9% at –0.3 V and decreased slightly at more negative potentials. On Fe-NCA, the peroxide yield was higher, around 15% at –0.3 V and decreased to 6% at high overpotentials. The peroxide production at metal-containing N-doped carbon aerogels is modest, which is advantageous for possible application of these materials as cathode catalysts for low-temperature fuel cells. At low overpotentials Co-NCA exhibits better selectivity to 4e\(^-\) reduction of O2, as confirmed also by the results of the Koutecky–Levich analysis.

The ORR activity of the non-precious metal catalyst-coated electrode depends on the catalyst loading, which needs to be optimised for the specific type of the catalysts. In Fig. 7, the RDE voltammetry curves of the electrodes of various Co-NCA loadings between 100
and 800 μg cm⁻² are compared. The half-wave potential of O₂ reduction shifts about 40 mV to negative direction as the catalyst loading decreases. In addition, the plateau currents are slightly lower for the lowest loading, which is related to lower n value (3.4 < n < 3.9, as revealed by the K–L analysis). This is in agreement with the results of the other studies, where increase in the peroxide yield with decreasing NPMC loading has been demonstrated [28,30].

The mass activity (MA) of the electrocatalysts studied was calculated as:

\[ MA = \frac{I_k}{m} \]  

where \( I_k \) is the kinetic current at a certain potential and \( m \) is the mass of the catalyst on the electrode. As expected, at −0.2 V the highest mass activity (14.1 A g⁻¹) was observed for the catalyst of lowest loading and it decreased as the loading increased, being 13.2 A g⁻¹, 8.5 A g⁻¹ and 4.9 A g⁻¹ for the electrodes covered with 200, 400 and 800 μg cm⁻² catalyst, respectively. This shows that in case of high loadings, the ORR process in the inner parts of the catalyst layer is partly limited by the diffusion of O₂. On the other hand, if the loading is too low, it would be difficult to obtain a homogeneous distribution of the catalyst on the electrode surface and this causes the apparent decrease in the value of n. In addition, in case of lower loading, there is a lower possibility of formed peroxide intermediate to resorb and to be further reduced, which can also cause lower value of n [28]. Considering this, 200 μg cm⁻² was chosen as the optimal catalyst loading for the materials involved in this study: although the value of MA was slightly lower than that of the lowest loading, the n value was more realistic. Similar loading has also been chosen as optimal for Fe-phenanthroline-based [23] and 4-aminoantipyrine-derived Fe-containing [28] porous catalysts. It must be noted, however, that various loadings, usually between 50 and 1000 μg cm⁻², have been used in the literature for studying the ORR on NPMCs by RDE method and the optimal loading undoubtedly depends on the nature of the catalyst material.
In order to demonstrate the effect of the presence of the transition metal during the pyrolysis of the aerogels on the ORR activity of the resulting materials, the RDE voltammetry curves of Co-NCA, Fe-NCA and NCA are presented in Fig. 8. It is evident that Co-NCA and Fe-NCA are both active electrocatalysts for ORR, the $E_{1/2}$ of the former being about 25 mV more negative compared to commercial Pt/C catalyst. NCA has much lower activity, the onset potential of $O_2$ reduction is about 80 mV and the $E_{1/2}$ value about 260 mV more negative than those of Co-NCA. The mass activity of NCA at $-0.2$ V is only 0.51 A g$^{-1}$, about 25 times less than that of Co-NCA. Furthermore, the peroxide yield is considerably higher for NCA and the value of $n$ is even lower than 3 at the potentials of $E > -0.7$ V (Fig. 5). At more negative potentials, however, the $n$ value increases and approaches to 4 at $-1.2$ V. It has also been shown before that the presence of transition metals during the pyrolysis results in more active NPMCs that display decreased peroxide yields in the ORR [15–17,24,35]. The role of metal-nitrogen coordinated centres (M-N$_4$/C) in the ORR electrocatalysis has recently been elucidated. It has been suggested that at these centres, the $O_2$ is first reduced to peroxide intermediate, which in alkaline solutions is further reduced to OH$^-$ on the same centres [43,44]. Comparison of the RDE voltammetry curves of Co-NCA and Fe-NCA shows that the onset potential of $O_2$ reduction is slightly more positive for Fe-NCA catalyst, however, the current increase is sharper for Co-NCA when potential is scanned to negative direction and at the potentials of $E < -0.15$ V, the activity of Co-NCA is higher. Therefore, the calculated mass activity for Fe-NCA at $-0.2$ V is 7.5 A g$^{-1}$, which is almost 2 times lower than that of Co-NCA.

The K–L analysis showed that the value of $n$ was also slightly lower for Fe-NCA at $E > -0.8$ V (Fig. 5). Very similar behaviour, the onset potential being higher for Fe-containing material, but smaller currents at more negative potentials, has been observed for graphene-based Fe- and Co-containing catalysts in alkaline solution [20] and NPMCs prepared from dicyandiamide in acidic medium [42]. However, Fe-containing NPMCs have very often displayed higher activities for ORR than their Co-containing counterparts [18,22,31], although Fe-containing N-doped carbon aerogel had slightly lower onset potential of $O_2$ reduction as compared to Co-containing materials [59]. Higher $O_2$ reduction catalytic activity of Fe-N$_2$C$_{4-x}$ centres as compared to Co-N$_2$C$_{4-x}$ has also been suggested by theoretical calculations [85]. However, in addition to the intrinsic properties of the active centres, the performance of the catalyst is determined by many factors, such as density of the active sites, morphological features of the catalyst etc. that may also be affected by the nature of the metal ion present in the synthesis. For instance, it has been suggested that in the synthesis of polyaniline-based NPMCs, Co is more effective than Fe in catalysing the decomposition of the precursor and formation of highly graphitic carbon structures [22].

The Tafel plots for $O_2$ reduction on Co-NCA and Fe-NCA are presented in Fig. 9. At low overpotentials (between $-0.1$ and $-0.2$ V), the Tafel slope is $-48$ mV for Co-NCA and $-70$ mV for Fe-NCA that further confirms the higher activity of the former. In alkaline solution, Tafel slopes in the range between $-50$ and $-70$ mV have usually been observed for Co- and/or Fe-containing N-doped NPMCs [20,38–41].

The stability of the catalyst is one of the key factors determining its applicability in fuel cells. For the first evaluation of the electrochemical stability of Co-NCA and Fe-NCA, repetitive potential cycling in $O_2$-saturated 0.1 M KOH for 1000 cycles between 0 and $-0.6$ V at 100 mV s$^{-1}$ was performed. Comparison of RDE voltammetry curves before and after potential cycling (Fig. 10) indicates...
slightly different behaviour of Co- and Fe-containing catalyst. For Co-NCA, about 10% decrease in the kinetic current at −0.2 V is observed, whereas for Fe-NCA, current increases with potential cycling (ca. 18%). The reason of this increase is not known at present, but such behaviour has been observed for Fe-containing NPMCs [19,21] and has been suggested to be due to the formation of iron oxides [21]. There was only a minor shift in the half-wave potential: about 3 mV to negative direction for Co-NCA and 3 mV of iron oxides [21]. There was only a minor shift in the half-wave potential: about 3 mV to negative direction for Co-NCA and 3 mV of iron oxides [21].

The metal-containing N-doped carbon aerogels have been successfully prepared by pyrolysis of organic aerogels that were obtained by sol–gel polymerisation of melamine, formaldehyde and 2,6-dihydroxy-4-methylbenzoic acid. The incorporation of Co and Fe ions into organic aerogel matrix was achieved by the ion exchange process. The aerogels showed promising electrocatalytic activity for ORR, low peroxide yield and good stability in alkaline solution and thus can be regarded as possible catalysts for alkaline fuel cells. Co-containing N-doped carbon aerogel was especially active, the half-wave potential of O₂ reduction on this material was only about 25 mV more negative compared to commercial Pt/C catalyst.

This work provides a facile approach towards carbon materials with tunable composition and pore structure that can be useful for a wide range of applications. N-doped carbon aerogels is a promising class of materials to be used as cathode catalysts for fuel cells and it is expected that future studies towards optimisation of the composition and surface morphology would allow for a further improvement of their electrocatalytic activity towards O₂ reduction.

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References


J. Kreek, M. Kulip, M. Uibu, A. Mere, M. Koel, Preparation of metal-doped carbon aerogels from local oil shale processing by-products, Oil Shale 31 (2014) 185–194.


