Electrocatalysis Using Porous Nanostructured Materials

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The performance of electrochemical reactions depends strongly on the morphology and structure of the employed catalytic electrodes. Nanostructuring of the electrode surface represents a powerful tool to increase the electrochemically active surface area of the electrodes. Moreover, it can also facilitate faster diffusive mass transport inside three-dimensional electrodes. This minireview describes recent trends in the development of synthesis routes for porous nanostructured electrode materials and discusses the respective important electrocatalytic applications. The use of structure-directing agents will play a decisive role in the design and synthesis of improved catalysts.

1. Introduction

Electrochemistry is enjoying growing interest in science and technology. In addition to established electrolysis processes such as the evolution of halogens, for example, chlorine,[1, 2] galvanic elements such as fuel cells, photoelectrochemical cells (PEC), or batteries have come to the fore in recent years. In particular, low-temperature fuel cells, such as polymer electrolyte membrane fuel cells (PEMFC)[3–5] or direct methanol fuel cells (DMFC)[6–8] enable efficient and direct electrochemical conversion of hydrogen or methanol into electricity. Hence, they represent key technology for the future production of electricity from renewable, clean, and sustainable resources. The widespread practical use of this technology requires the development of more efficient processes and, in particular, new efficient electrocatalysts. Moreover, a deeper understanding of the reaction mechanisms and kinetics is also important to improve the electrocatalytic performance.

The efficiency of an electrocatalytic reaction is expressed as the overpotential, η (sum of losses of electric potential), that is, the difference between a theoretical potential required for a catalytic reaction and the potential required in the practical experiment. These losses result from different physicochemical phenomena, for example, kinetic reaction overpotentials and ohmic overpotentials. Ohmic overpotentials are a consequence of electric resistance of the electrolyte, transport limitations of charged reactant species, and conductor and contact resistances. Minimizing these overpotentials is one of the main challenges for electrochemists in the development of efficient electrocatalysts. However, such optimization requires a fundamental understanding of all individual steps that contribute to an electrocatalytic process.

Scheme 1 illustrates an example of a porous electrode and the sequence of coupled physicochemical steps that constitute an electrocatalytic process. The chemical transformation of reactants occurs in the reaction layer near the surface of the electrode. The catalytic reaction itself proceeds at the interface between (accessible) the electrode surface and electrolyte. It consists of adsorption, reaction, and desorption. However, these catalytic steps are often preceded by diffusive transport.

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Porous electrocatalysts have been synthesized in many different ways. Synthesis methods include chemical reduction or electrochemical deposition from metal salt solutions, deposition by sputtering or precursor evaporation, sol–gel synthesis, powder technology, or spraying and dip-coating methods. However, the degree of porosity and control over the electrocatalyst nanostructure varies significantly between the different synthesis methods.

This minireview focuses on synthesis methods that enable direct control over the catalyst nanostructure through physical synthesis parameters or with auxiliary structure-directing agents. Synthesis options for porous catalysts and porous catalyst supports are described in Section 2. Moreover, the role of the nanostructure in improving the performance of the electrocatalysts is discussed for three selected reactions in Section 3.
2. Synthesis of Porous Nanostructured Electro catalysts

The synthesis of porous nanostructured electrocatalysts can be realized by nanostructuring of either the conductive support (mostly carbon) or the electrocatalytically active material (mostly metals or metal oxides). Possible synthesis routes for nanostructured electrocatalysts described below are 1) nanocasting by using templates, 2) dealloying of alloys, and 3) electroassisted deposition or dissolution.

2.1. Nanocasting with Templates

Nanocasting is the process in which a template with a length scale of nanometers is surrounded or filled with the material (or a precursor for it) to be cast. The initial template is removed thereafter from the stabilized precursor phase, thereby a material with open porosity can be obtained. Different templates allow precise control over the synthesized porous structures. In a review from 2010, Walcarius highlighted recent trends for template-directed porous electrodes in the field of electroanalysis.

The following part focuses mainly on the use of soft templating synthesis strategies that lead to porous templated electrocatalysts and are highlighted by a few examples.

Figure 1 illustrates the nanocasting concept of using micelles of amphiphilic polymer molecules as soft templates. Upon deposition, the micelles assemble into well-defined periodic mesostructures, such as hexagonal or cubic phases, in which the voids between the micelles are filled with the precursor (Figure 1I). Subsequent treatment of the composite removes the template (typically by template extraction or heat treatments) and results in mesoporous materials (Figure 1II).

The general concept allows the synthesis of both mesoporous carbon and metal oxides. The precursor used (organic precursors for carbon and metal alkoxides or metal salts for metal oxides) and synthesis conditions permit the synthesis of mesoporous bulk catalysts (Figure 1II; e.g. Pt, Pt/Ru, RuO2, IrO2) or mesoporous catalyst supports with incorporated active species (Figure 1IIa; e.g. Pt in carbon, Pt-Pb in carbon/Nb2O5). The mesoporous material (Figure 1II) resulting from soft templating can itself be replicated again; this material then acts as a “hard template” (Figure 1III). The hard template, for example, mesoporous silica SBA-15, is infiltrated with a precursor. After template removal (by HF in the case of silica), a negative mesoporous replicate (Figure 1III) is obtained, which resembles the initial structure of the soft templates (Figure 1II).

In analogy to the soft-templated route, mesoporous electrocatalytic active materials (Figure 1III; Pt-Ru) or mesoporous supports (Figure 1IIla) can be achieved. Such mesoporous supports obtained by the hard-templating pathway (Figure 1IIla) are, for example, OMCs, which are widespread in the field of nanostructured electrocatalysts (see Sections 3.1 and 3.2). Nevertheless, carbon-free, hard-templated mesoporous WO3 was also successfully used as a nanostructured electrode catalyst support.

Examples of materials obtained by the nanocasting approach are given in Figure 1 for both the synthesis of bulk catalysts (A and B) and support materials with incorporated active components (C, D). Figure 1A illustrates a TEM image of a mesoporous iridium oxide film prepared by the soft-templated preparation pathway (Figure 1II). The iridium oxide film was obtained by dip-coating through deposition of iridium acetate precursor and PEO-b-PB-b-PEO polymer templates on titanium electrodes. After heat treatment at 300 °C, the soft-template decomposed and iridium oxide with a cubic mesostructure with pore sizes of 16 nm and a specific surface area of 248 m² g⁻¹ (Kr-BET) was obtained. The catalytic performance of templated versus untemplated IrO2 catalyst in the oxygen evolution reaction (OER) is discussed in Section 3.3.

Figure 1B shows a TEM image of Pt–Pb nanoparticles incorporated into the pores of a mesoporous niobium oxide–carbon composite support. The synthesis procedure reported by Orillall et al. is based on the self-assembly of Pt-b-PEO block copolymer templates with NbCl5/Nb(OEt)5 and noble-metal precursors [(dimethylcyclooctadiene)platinum and triphenylphenehydrol]lead. After heat treatments (700 °C under argon and subsequently 875 °C under reductive atmosphere), a crystalline, hexagonally arranged, cylindrical, mesoporous niobium oxide–carbon composite with Pt–Pb nanoparticles incorporated into the mesopores was obtained. The materials synthesized in one pot show pores with an average diameter of around 25 nm and specific surface areas (N2-BET) between...
137 and 217 m² g⁻¹. These electrocatalysts show promising electrochemical activity toward formic acid oxidation.

The TEM image in Figure 1C presents a nanostructured Pt–Ru electrocatalyst synthesized through the hard-templating approach (Figure 1III), reported by Jiang and Kucernak. First, they synthesized hexagonal mesoporous SBA-12 silica using nonionic surfactant Brij 76 as the soft template and tetraethoxysilane (TEOS) as the silica source. After calcination a mesoporous silica hard-template was obtained. Subsequently, H₂PtCl₆ and RuCl₃ were impregnated into the silica template and heat-treated at 300 °C. Thereafter, the silica template was removed by using a solution of 10 wt% HF at room temperature. The retained nanostructured Pt–Ru material with mesopores of about 3 nm in diameter demonstrates high activity towards the electrochemical oxidation of methanol.

Figure 1D shows a TEM image of an OMC film with incorporated Pt nanoparticles (synthesis path IIIa). Here, Su et al. first prepared hexagonal mesoporous silica SBA-15 with the surfactant P123 and a SiO₂ precursor. The calcined mesoporous SBA-15 hard template was impregnated with benzene (carbon source) by chemical vapor deposition (CVD). After carbonization at 900 °C the silica hard template was then removed with HF solution. Platinum nanoparticles were then deposited on the prepared mesoporous carbon by the borohydride reduction method. The enhanced activity of this material in electrochemical methanol oxidation is described in Section 3.2.

In addition to templating routes that start with amphiphilic molecules, porous anodic aluminum oxide (AAO) hard templates can also be used for the preparation of nanostructured electrocatalysts. For example, Zhao et al. used AAO templates for the synthesis of Pt–Ru and Pt nanowire array electrodes on Ti/Si substrate. This catalyst synthesis started with the preparation of the AAO template by anodization of a thin Al film on a conductive Ti/Si substrate in oxalic acid solution at 20 V (see also Section 2.3). The resulting AAO template contained uniform cylindrical pores that were aligned perpendicular to the substrate surface. The pores were then filled with a metal by electrodeposition from an electrolyte solution containing, for example, H₂PtCl₆ and RuCl₃. A platinum plate was used as a counter electrode and the AAO/Ti/Si structure was the working electrode. The as-prepared composites were immersed in a solution of NaOH to remove the AAO template. The brush-shaped Pt–Ru nanowires obtained were about 30 nm in diameter and 1 μm in length. They were tested for methanol electro-oxidation. Figure 2A shows a SEM image of the surface morphology of the prepared Pt–Ru nanowires. In a similar way, Liu et al. used AAO hard templates to synthesize multisegmant Pt–Ni nanorods as methanol electro-oxidation catalysts by sequential electrodeposition of Pt and Ni into nanoporous anodic alumina membranes.

Moreover, Alia et al. used silver nanowires as hard templates to synthesize porous platinum nanotubes for oxygen reduction and methanol oxidation reactions. The porous platinum nanotubes, with a thickness of 5 nm, an outer diameter of 60 nm, and a length of 5–20 μm, were synthesized by galvanic displacement of silver nanowires, which were formed by ethylene glycol reduction of silver nitrate. Figure 2B shows a TEM image of the respective templated electrocatalysts.

In the case of a nanostructured electrocatalyst with regular pore sizes above 50 nm, spherical latex templates (e.g. polymer or silica spheres) can be employed. These spheres are assembled into colloidal crystals with highly uniform 3D structures and are then infiltrated with a carbon or metal oxide precursor. Alternatively, the spheres and the precursor are codeposited. Thereafter, the template is usually removed by calcination (polymer) or HF etching (SiO₂) to produce porous catalysts or carbon supports. Chai et al. synthesized ordered, uniform, porous carbon frameworks with pore sizes in the range of 10 to 1000 nm by infiltration of colloidal SiO₂ templates with phenol and formaldehyde (carbon source) followed by polymerization and carbonization of the carbon precursor. The porous carbons were used as supports for Pt–Ru alloy nanoparticles in methanol fuel cell catalysts. Figure 3A shows a TEM image of this catalyst. Furthermore, Su et al. synthesized polystyrene-templated macroporous silica as a hard template to deposit carbon on the surface of this inverse silica opal. The carbon deposition was carried out by using a CVD method. The macroporous carbon was then used as a support for Pt–Ru alloy nanoparticles and showed strong performance improvements in the methanol oxidation reaction due to nanostructuring of the catalyst support (see Section 3.2). Figure 3B shows a
TEM image of the hollow carbon spheres with a diameter of around 200 nm with incorporated platinum nanoparticles.

It is clear that, in contrast to the soft-templated synthesis route, the hard-templating approach demands more preparation steps. However, hard templates are often more stable against the precursor system and a precise negative replica of the template can be created more easily than with soft templates. In general, nanocasting of templates is one of the most promising synthesis strategies to precisely control the porous structure of nanostructured electrocatalysts.

### 2.2. Nanoporous Materials Made by Dealloying

Another important synthetic process to obtain 3D highly porous electrocatalytic electrodes is chemical dealloying (CD). In this synthesis single-phase, multicomponent bulk alloys are formed by melting. From this alloy, the less-noble metal is selectively dissolved by an etching process in acids, alkali, or electrochemically. The removal of the less-noble metal can result in mesopores being formed in the remaining metal. The synthesis of mesoporous electrocatalysts by chemical or electrochemical dealloying has, for example, been reported for Au from an Ag–Au alloy, Pt from Cu–Pt, Si–Pt, Cu from Mn–Cu, and Al–Cu, and Ag from Al–Ag. Control over the size of the mesopores during electrochemical or chemical dealloying results from varying the starting alloy composition, the electrochemical potential driving dissolution, the electrolyte temperature, the dealloying/etching time, or employing thermal annealing after dealloying. A potential drawback of the synthetic method is the fact that complete removal of the alloying compound cannot be guaranteed; hence, the second metal might also affect the electrochemical performance of the resulting catalysts.

Typical electron microscopy images of nanoporous gold films made by dealloying from different Ag–Au alloys are presented in Figure 4. Figure 4a depicts a cross-sectional SEM image of dealloyed Au$_{32}$Ag$_{68}$ which shows an open porosity in the whole film. The planar view of a dealloyed Au$_{26}$Ag$_{74}$ film (Figure 4b) indicates ligament spacings in the order of 10 nm.

The dealloying method described can also serve for the synthesis of a support such as porous gold. When compared with typical carbon supports, the deposition of an atomically thin layer of platinum on gold can improve the catalyst/substrate binding while providing a high dispersion of the active platinum phase. Furthermore, it is possible to use the dealloyed porous material as a hard template for the nanostructuring of platinum-based electrocatalysts formed by epitaxial casting. An epitaxial skin of a second material is coated on a mold that is subsequently dissolved away. In this case platinum is grown epitaxially onto the nanoporous gold by an electrolysis plating process described by Ding et al.[30] This is a simple strategy to synthesize free-standing noble-metal membranes with a hierarchical bicontinuous porous architecture.

With dealloying it is possible to synthesize porous 3D catalysts in a simpler and faster way than with the templating techniques described in Section 2.1. However, the synthesis of ordered nanopore structures by dealloying has not been reported so far.

### 2.3. Electrochemical Deposition and Dissolution

For some electrode compositions, material-specific synthetic routes for nanostructures exist. This includes, in the case of titanium, the electrochemical dissolution of titanium to create TiO$_2$ nanorods; metals such as platinum can also be nanostructured by electrochemical deposition in the presence of structure-directing agents.

Schmuki et al. synthesized highly ordered, self-organized TiO$_2$ nanotubes by electrochemical anodization of titanium.[45–47] This synthetic route represents a simple electrochemical reaction of a metallic titanium substrate under specific conditions, such as a sufficient anodic voltage and acidic fluoride (0.05–0.5 M) containing electrolytes. However, oxide nanotubes with well-defined lengths and diameters and vertical alignment relative to the substrate are obtained. The defined nanostructure results from varying the pH of the electrolyte (influences the thickness of the tube walls), the voltage (diameter of the tubes), or anodization time (tube length). Figure 5 shows one example of TiO$_2$ tubes obtained by electrochemical anodization of a titanium foil in 0.135 M HF in ethylene glycol electrolyte at 30 V for 5 h. After anodization the sample was annealed in air for 1 h at 450 °C. Macak et al.[45] demonstrated the influence of TiO$_2$ nanotubes as supports for Pt/Ru nanoparticles in the methanol oxidation reaction.

Electrochemical and hydrothermal methods can be combined to synthesize porous platinum electrodes. In the hydro-
thermal-assisted seed growth method,\textsuperscript{[52]} platinum particles are first deposited electrochemically on titanium substrates without structure-directing agents. Thereafter, porous platinum structures were reported to grow by hydrothermal treatment of these substrate for 10 h at 100 °C using autoclaves containing ethylene glycol, a platinum salt (H$_2$PtCl$_6$), and HCl, for example.\textsuperscript{[53]}

Nanostructured (mesoporous) electrodes of metals such as Pt\textsuperscript{[54,55]} and Au\textsuperscript{[56,57]} can also be synthesized by electrochemical deposition through electroreduction of a metal salt in the presence of hard or soft templates, such as silica colloids,\textsuperscript{[56,57]} polystyrene (PS) particles,\textsuperscript{[57]} or micelles of octaethylene glycol monohexadecyl ether (C$_{16}$EO$_8$)\textsuperscript{[54,55]} (see Section 2.1). Moreover, ruthenium oxide\textsuperscript{[58]} was synthesized in a similar way; however, in this case, the structure-directing agent was polystyrene. Methanol oxidation on porous platinum catalysts was studied by Garcia et al.\textsuperscript{[55]}

In many syntheses it is necessary to use a templating method before the electrochemical deposition of the electrocatalytic active material can be carried out. Therefore, numerous preparation steps are needed; however, precise control of the pore diameters and layer thickness is possible. In the case of anodization, only a 1D structure could be synthesized. Advantages of this method are the precisely tunable tube lengths and diameters and also direct electrical connectivity between the substrate and support or catalytically active material due to direct growth of the tubes from the substrate.

### 3. Applications as Electrocatalysts

A complete overview of all reported applications of nanostructured electrocatalysts is beyond the scope of this minireview. However, we focus on three selected electrochemical reactions, namely, oxygen reduction, methanol oxidation, and oxygen evolution, to illustrate the advantages of the nanostructured electrodes. Two of these examples employ supported catalysts, namely, the oxygen reduction reaction (Section 3.1) and methanol oxidation (Section 3.2), whereas the oxygen evolution reaction uses the unsupported catalyst IrO$_2$ (Section 3.3).

#### 3.1. Oxygen Reduction Reaction on Carbon-Supported Platinum

One of the most serious challenges in the development of proton-exchange membrane fuel cells (PEMFC) is the oxygen reduction reaction (ORR). ORR is a complex electrode reaction due to its irreversibility and the very slow kinetics. Two possible reaction pathways for the ORR exist: the direct 4-electron reduction reaction (ORR). ORR is a complex electrode reaction due to its irreversibility and the very slow kinetics. Two possible reaction pathways for the ORR exist: the direct 4-electron reduction pathway [Eq. (1)]:

$$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad (1)$$

and the two-electron reduction pathway with hydrogen peroxide as an intermediate [Eqs. (2) and (3)]:

$$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 \quad (2)$$

$$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad (3)$$

Platinum-based materials are the most commonly used catalysts for ORR,\textsuperscript{[4,5,59]} often in the form of unsupported large crystalline platinum black particles.\textsuperscript{[60]}

A decrease in the platinum loading was achieved by the introduction of carbon black as a catalyst support (commercial Pt/C).\textsuperscript{[51,62]} Due to the high surface area of carbon black, better spatial distribution and utilization of the active platinum particles were achieved. However, the ORR activity of a catalyst also depends significantly on the size of the platinum particles and the spatial distribution of these particles over the support.\textsuperscript{[63]}

Despite the high surface area of carbon black, two main disadvantages exist: Due to its dense structure carbon black supports show significant mass-transfer limitations. Moreover, they also undergo thermal degradation at high fuel-cell working temperatures.\textsuperscript{[64,65]}

A significant improvement in the ORR performance can be achieved by using nanostructured carbon supports, as summarized in a review by Antolini.\textsuperscript{[62] In particular, OMC\textsuperscript{[62,66–70]} attracted great attention as a catalytic support material for ORR due to their controllable pore sizes and high surface areas (see Section 2.1). Higher spatial distribution of the active nanoparticles and more facile diffusion of reactants and products due to the mesoporous structure led to an increase in the catalytic performance. Figure 6 demonstrates the activity increase of ORR on OMC supports. The OMC support was synthesized by hard templating with SBA-15 mesoporous silica. Sucrose was used as the carbon source. At an identical Pt loading and comparable Pt particle size, the OMC-supported Pt catalyst clearly shows enhanced ORR activity compared with the standard Pt/C catalyst. At a potential of about 0.55 V versus SCE [\textapprox{} 0.31 V vs. a reversible hydrogen electrode (RHE)] the current
3.2. Methanol Oxidation on Carbon-Supported Platinum

DMFCs are promising highly efficient and clean energy sources for applications in electric vehicles and portable devices. The oxidation of methanol is an important reaction for the design of DMFCs. The total oxidation process of the methanol oxidation can be written as shown in Equation (4):

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^{-}
\]

(4)

This total oxidation process can be divided in the three conventional reactions for a platinum catalyst shown in Equations (5), (6), and (7):[72]

\[
\begin{align*}
\text{Pt} + \text{CH}_3\text{OH} \rightarrow \text{Pt}-\text{CO} + 4\text{H}^+ + 4\text{e}^- & \\
\text{Pt} + \text{H}_2\text{O} \rightarrow \text{Pt}-\text{OH} + \text{H}^+ + \text{e}^- & \\
\text{Pt}-\text{CO} + \text{Pt}-\text{OH} \rightarrow 2\text{Pt} + \text{CO}_2 + \text{H}^+ + \text{e}^- &
\end{align*}
\]

(5) (6) (7)

A typical cyclic voltammogram for the oxidation of methanol on platinum is shown in Figure 7.

The cyclic voltammetry profiles show that, at a potential of around 0.2 V versus SCE, methanol molecules adsorb at the platinum surface [Eq. (5)]. Water is oxidized at a potential of about 0.4–0.45 V vs. SCE [Eq. (6)]. If both species are adsorbed on the surface, then the formation of CO₂ can occur [Eq. (7)], as indicated in the cyclic voltammogram by the increase in the potential in the forward scan at this point (see Figure 7). Due to the current density of Pt–OH or Pt–O, the current density reaches a maximum value and decrease thereafter (≈0.6–0.7 V vs. SCE). MeOH decomposition and CO removal do not proceed efficiently on Pt–O surfaces. In the back scan, CO desorption starts at a potential of about 0.7 V vs. SCE and reaches a maximum current density at around 0.4 V vs. SCE. The onset potential and current density at a selected potential are important for the comparison of different catalysts. Lower onset potentials correspond to better catalysts.

Much effort has been made to enhance the performance of methanol oxidation. One method was the improvement of electrocatalytic activity and minimization of CO poisoning due to the use of Pt–Ru alloys or other metals or metal alloys.[73–75] Furthermore, great work has been made to improve access to large areas of the catalytic material, as well as facilitate electron transfer and mass transport due to structuring and well-developed porosity of the support.

The standard catalytic activities of platinum catalysts on carbon black (Pt/C) were determined by different groups.[6,8,76,77] Results given in Table 1 show that specific current densities with relation to the electrochemical surface area (ECSA) are between 0.1 and 0.4 mA per cm² of Pt at 0.7 V versus RHE for standard Pt/C catalysts. The onset potential is around 0.6 V versus RHE.

For catalysts with an OMC support, the onset potential is slightly lower (≈0.1 V) and the specific current density is around 0.4 mA per cm² of Pt, which is higher than the values for a commercial catalyst (Table 1). Su et al.[28] demonstrated that catalysts with ordered meso- and macroporous carbon

### Table 1. Catalytic activity of methanol oxidation for Pt (20 wt%) on OMC supports and commercial carbon at room temperature.

<table>
<thead>
<tr>
<th>Synthesis procedure of PtX/C and PtX/OMC</th>
<th>Onset potential [V] vs. RHE</th>
<th>j [mA per cm² of Pt] at 0.7 V vs. RHE</th>
<th>c₅₀</th>
<th>/[[mol L⁻¹]]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>commercial Pt/C (E-TEK)</td>
<td>≈0.5</td>
<td>≈0.15</td>
<td>1</td>
<td></td>
<td>[28]</td>
</tr>
<tr>
<td>commercial Pt/C (E-TEK)</td>
<td>≈0.6</td>
<td>≈0.1</td>
<td>1</td>
<td>[6]</td>
<td></td>
</tr>
<tr>
<td>hard templating with silica opal, CVD for 2 h at 1000 °C</td>
<td>≈0.45</td>
<td>≈0.4</td>
<td>1</td>
<td>[28]</td>
<td></td>
</tr>
<tr>
<td>hard templating with SBA-15, CVD for 1 h at 900 °C</td>
<td>≈0.55</td>
<td>≈0.3</td>
<td>1</td>
<td>[9]</td>
<td></td>
</tr>
<tr>
<td>hard templating with SBA-15, CVD for 60 min at 500 °C and graphitization at 850 °C</td>
<td>≈0.55</td>
<td>≈0.63</td>
<td>1</td>
<td>[14]</td>
<td></td>
</tr>
<tr>
<td>hard templating with SBA-15, wet impregnation, functionalization in 2M HNO₃ for 0.5 h</td>
<td>≈0.6</td>
<td>0.5</td>
<td></td>
<td></td>
<td>[7,28]</td>
</tr>
</tbody>
</table>

Figure 7. Typical cyclic voltammograms for the electro-oxidation of methanol at platinum catalysts in 0.5 M H₂SO₄ + 1 M CH₃OH at room temperature. Pt/XC-72 is a commercial catalyst and Pt/CMK-5-x-60 are synthesized ordered porous carbons, in which the last number denotes the graphitization time and the second number is the graphitization temperature. Potentials are given versus SCE (reprinted with permission from ref. [16]).
supports (pore size: \( \approx 3.5 \) \( \text{nm} \) and \( \approx 70 \) \text{nm}, respectively) had a higher electrocatalytic activity towards methanol oxidation than standard catalysts. This results from better mass transport of the reactants and products due to higher spatial distribution of platinum particles on the mesoporous material. Lei et al.\(^{[16]} \)
also showed that the electrocatalytic activity of Pt supported on OMC (pore size \( \approx 3–4.7 \) \text{nm}) was higher than that of standard catalysts. Moreover, Calvillo and co-workers reported that functionalization with \( \text{HNO}_3 \) to create oxygen groups at the surface of OMC improved the performance of methanol oxidation due to better spatial distribution and anchoring of the platinum particles on the support.\(^{[7, 20]} \)

This short summary of OMCs as one example of a porous nanostructured catalyst support for methanol oxidation shows that the characteristics of the carbon support for platinum catalysts have great impact on electrochemical properties in methanol oxidation. The OMCs offer a larger accessible surface area than that of standard carbon blacks; this results in better spatial distribution of the platinum particles on the support and enhances catalytic activity. Furthermore, the area of the electrode/electrolyte interface increases, which enhances charge and mass transport through the porous Pt/OMC catalyst and decreases the diffusion distance of electrolyte ions.

3.3. OER on Unsupported IrO\(_2\)

OER is the anodic half-cell reaction of the water-splitting process. The efficient oxidation of water is a great challenge in the development of viable, cost-effective, durable technologies for the conversation of light into storable fuels. The electrochemical water-splitting reaction is divided into two half-cell reactions. The hydrogen evolution reaction (HER) proceeds at the cathode and the OER at the anode. The oxidation process is shown in Equation (8):

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad (8)
\]

OER is a very complex process with several surface-adsorbed intermediates and the mechanism of OER on these different electrodes is still a matter of discussion. More detailed information about the water-splitting reaction and it half-cell reactions can be found in a recent review by Dau et al.\(^{[78]} \)

Among numerous catalytic materials, such as binary and ternary ruthenium metal alloys,\(^{[79, 80]} \) ruthenium oxides, or ruthenium mixed metal oxides,\(^{[81–84]} \) iridium oxide is regarded as one of the most stable and active catalysts for the OER.\(^{[15, 85–89]} \) Recent studies on the synthesis of colloidal iridium oxide nanoparticles\(^{[85, 87, 90]} \) reported an increase in the electrochemically active surface area and a reducing OER overpotential. Iridium particles were deposited on the electrode support. The overpotential for the OER, determined at a current density of 0.5 A cm\(^{-2} \), was around 0.25 V versus RHE, as reported by Nakagawa et al.\(^{[87]} \) However, synthetic method did not provide access to controlled pore structure and crystallinity of the layers. Recently, we highlighted a soft-templated synthesis of nanocrystalline mesoporous iridium oxide catalyst layers. The mesoporous IrO\(_2\) catalyst layers were synthesized by soft-templating methods with polymer micelles, as described in Section 2.1. Soft templating created mesopores of about 16 nm in diameter, as shown in Figure 1.A.

Figure 8A provides information about the active surface area of the film, which was determined electrochemically in a potential window between 0.4 and 1.4 V versus RHE.\(^{[15]} \) The templated mesoporous (Figure 8A, a) film exhibits a significantly larger active surface area than the untemplated IrO\(_2\) sample (Figure 8A, b). Figure 8B shows cyclic voltammograms of the OER recorded on IrO\(_2\) films with and without templated mesoporosity. These voltammograms were recorded under quasi-steady-state voltammetric responses (scan rate 6 mVs\(^{-1}\)). Both catalysts are active for OER; however, the templated mesoporous catalyst clearly shows a higher catalytic activity per geometric surface area of the planar electrode (see Figure 8B). Therefore, the improved performance of the templated meso-
porous catalyst in Figure 8B originates from an increase in the accessible surface area.

4. Summary and Outlook

Nanoporous conductive porous materials are attractive candidates as supports or active components of catalytic electrodes. The porous nanostructure significantly increases the catalytically active surface area and accelerates mass transport; hence, porous electrodes are particularly beneficial for gas reactions in gas diffusion electrodes. Beyond the examples discussed herein, porous electrodes are also suited for gas reactions such as hydrogen evolution and reduction, formic acid formation,\(^\text{31}\) CO and glucose oxidation, or the chlorine evolution reaction. In most cases, the intrinsic catalytic activity is not influenced by the structuring of the electrode support or the catalytic species.

Depending on the detailed nature of the reacting molecules, mass transport and diffusion rates, optimum pore diameters, wall thicknesses, and catalyst or support morphologies may differ significantly. Hence, individual optimization of the electrode material is required for each application. We have emphasized three different synthetic routes that are applicable for the synthesis of well-ordered, porous, nanostructured electrode materials. Close collaboration between material scientists and electrochemists will promote new promising developments in the field of porous nanostructured materials as highly active electrocatalysts.

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