

# Electrodes Functionalized with the 2,2,6,6-Tetramethylpiperidinyloxy Radical for the Waste-Free Oxidation of Alcohols

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Electrodes functionalised with the organocatalyst 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) moiety hold great potential for the development of waste-free industrial synthesis of valuable carbonyl compounds using electrons and alcohols as the only reactants. Since the inception of the first active electrode in 1988, a number of different electrodes have been developed

to the recent fastest TEMPO-mediated alcohol oxidation process ever reported. In addition to good activity and broad applicability to different substrates, the electrode stability is the crucial factor that will guide the adoption of this eminently clean technology by the fine chemical and pharmaceutical industry.

## Introduction

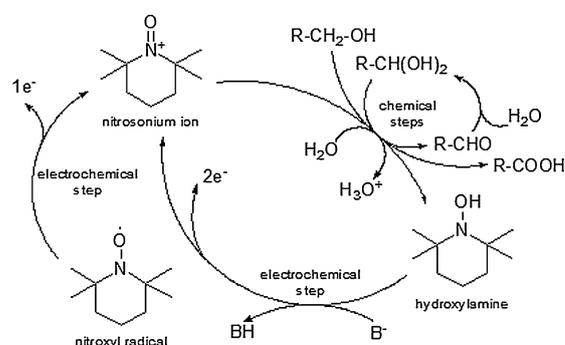
Electrochemical synthetic processes are highly desirable for the oxidation and reduction of organic compounds as they afford the desired substance directly with an electric current to replace redox reagents, which thereby prevents the formation of undesired waste.<sup>[1]</sup> A few, though very important, organic electro-syntheses are performed on an industrial scale, which include the 340 000 tonne year<sup>-1</sup> production of the adiponitrile precursor of Nylon-6,6<sup>[2]</sup> and the production (without mediator) of aryl aldehydes by the oxidation of toluene on a 5000 tonne year<sup>-1</sup> scale.<sup>[3]</sup>

The number of industrial applications, however, is growing along with the interest of fine chemicals and pharmaceutical companies as more selective electro-syntheses are developed,<sup>[4]</sup> concomitant with the increased demand of greener industrial processes. For instance, as early as of 2010, leading practitioners who summarised achievements in organic electrochemistry<sup>[5]</sup> described reactions performed in ionic liquids, the electro-generation of reactants, reactions that use renewable starting materials (biomass), green organic electro-syntheses in microemulsions as well as the synthesis of complex molecules using an electro-synthetic key step.

In this context, the development of an efficient electrochemical route for the selective oxidation of alcohols would be particularly desirable, as aldehydes and ketones are used widely as drugs, drug precursors, cosmetics, fragrances and aromas in products in which contamination with transition metals gener-

ally employed as reaction catalysts is subject to stringent limits.<sup>[6]</sup>

A metal-free route, today employed widely by industry,<sup>[7]</sup> makes use of the highly selective and versatile organocatalysts that are the stable di-tertiary-alkyl nitroxyl radicals, such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) along with a primary oxidant such as NaOCl under buffered alkaline conditions for the regeneration of the active oxoammonium salt from the hydroxylamine (Scheme 1).



**Scheme 1.** Electrochemical oxidation of a primary alcohol mediated by TEMPO.

In an eminent example of indirect electrolysis in which an electrode reaction is employed to maintain a reagent in the appropriate oxidation state, in TEMPO-mediated oxidations the cyclic oxoammonium ion is generated in situ electrochemically by applying a small electric potential (0.7 V vs. Ag/AgCl) to a solution of nitroxyl radicals. Different alcohols, typically dissolved in a water and organic solvent mixture, are then converted in good yield and selectivity to carbonyls<sup>[8]</sup> or sugars in water to valued glucuronates.<sup>[9]</sup> Remarkably, the electro-oxidation of alcohols to carbonyls can be performed with *N*-oxyl radicals and

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the substrate alcohol adsorbed onto silica gel microparticles without organic solvent.<sup>[10]</sup>

The widely accepted oxidation mechanism involves the oxoammonium ion that oxidises the alcohol function and is then regenerated either electrochemically from the hydroxylamine or, in solution by a comproportionation reaction of the latter species with unreacted TEMPO (Scheme 1).<sup>[11]</sup>

The electrochemical approach catalysed heterogeneously was first proposed by Osa et al. in 1988, who functionalised a graphite felt electrode surface with nitroxyl radicals covalently attached to poly(acrylic acid) (PAA) coated on the electrode.<sup>[12]</sup> Under a controlled potential of 0.8 V (vs. the saturated calomel electrode; SCE) and in the presence of the base 2,6-lutidine and NaClO<sub>4</sub> dissolved in acetonitrile, the electrode oxidised nerol to neral selectively in approximately 50% yield with a turnover number > 1560.

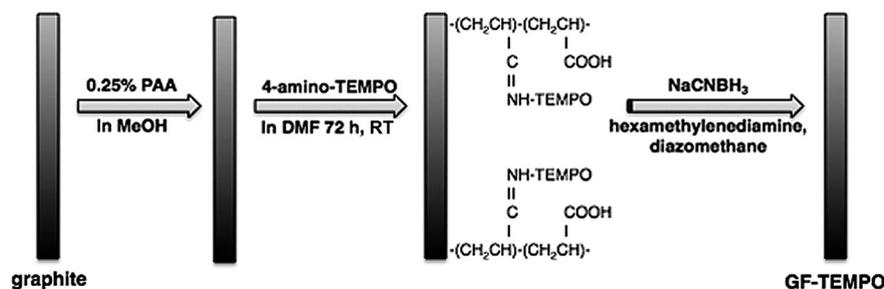
The proof-of-concept was established. Alcohols could be oxidised in organic solvent with no waste formation, which avoided the use of any chemical oxidants.

Since then, numerous new electrodes functionalised with *N*-oxyl radicals have been developed for preparative purposes until the recent development of an electro-active organocatalyst of unprecedented activity amongst TEMPO-mediated oxidations under chemical, electrochemical, or aerobic oxidation conditions reported previously.<sup>[13]</sup>

In the following, we describe the advances that led to such achievements from a nanochemistry perspective, namely, we emphasise how the hurdles posed by the first catalytic electrodes were overcome using the “bottom-up” approach by which the properties of the functional material are designed to ensure the optimal diffusion of reactants, broad reaction scope and enhanced electrode stability. We conclude by providing arguments that justify our viewpoint that sol-gel electrodes functionalised with TEMPO will soon find practical application in the selective oxidation of alcohols.

### Polymeric electrodes

As mentioned above, the methylated graphite electrode modified with TEMPO (GF-TEMPO) developed in the late 1980s by Osa et al. could be used to mediate the selective oxidation of nerol to neral in CH<sub>3</sub>CN in the presence of 2,6-lutidine as the base and NaClO<sub>4</sub> as the electrolyte.<sup>[12]</sup> In detail (Scheme 2), a carbon felt electrode was coated with a thin layer of PAA that was derivatised with 4-amino-TEMPO and then cross-linked by a successive reaction with methylenediamine to form a hydrophobic network that is instrumental to protect the heterogenised TEMPO moiety. Subsequent treatment with diazomethane ensures the methylation of the remaining –COOH groups, which would otherwise promote the decomposition of the oxoammonium ions.



Scheme 2. The route to TEMPO-modified graphite felt electrodes developed by Osa and co-workers (Adapted from Ref. [14], with kind permission).

With the aim to explain the enhanced stability of the methylated electrode out of many obtained using alkylenediamines up to hexamethylenediamine, Osa suggested that the “increasing hydrophobicity in the domain of the PAA layer”<sup>[14]</sup> stabilises the TEMPO-modified electrode towards macro-electrolysis, namely, deactivation caused by the conversion of the oxoammonium ion to inactive species.

Tokuda and co-workers used PAA to functionalise a glassy carbon rotating electrode with 4-amino-TEMPO to target the electro-oxidation of 4-methoxybenzyl alcohol dissolved in acetonitrile.<sup>[15]</sup> Along with NaClO<sub>4</sub> as the electrolyte, the base 2,6-lutidine was again crucial to promote the alcohol oxidation. An ultra-thin polymeric monolayer (TEMPO coverage  $\approx 10^{-10}$  mol cm<sup>-2</sup>) was required for a reasonable reaction rate as the electron transfer was severely limited with multiple PAA layers (TEMPO coverage  $\approx 10^{-9}$  mol cm<sup>-2</sup>). No mention of the electrode stability was made.

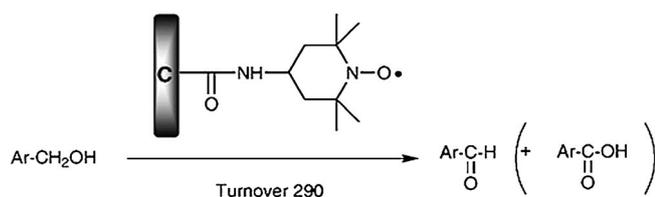
In continuation of the investigation on catalytic electrodes with polymeric coatings, in 2001 Belgsir and Schäfer immobilised the TEMPO moiety onto water-stable Nafion to attempt the oxidation of carbohydrates in carbonate solution buffered at pH 10.<sup>[16]</sup> In the first electrocatalytic reaction run, the catalyst was active and selective, but the nitroxyl radical density decreased rapidly because of catalyst degradation.

In 2005, Geneste et al. described a simple method to form a sub-monolayer of nitroxyl radicals tethered chemically (surface concentration around  $10^{-10}$  mol cm<sup>-2</sup>) to the surface of a graphite electrode by binding the radical through an amide link to a graphite felt electrode (Scheme 3).<sup>[17]</sup>

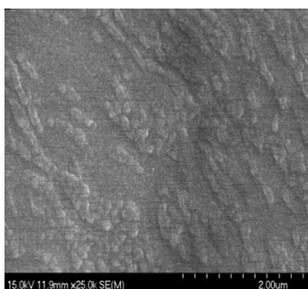
Again, in the first run the electrode was catalytically active in both organic and aqueous media. However, the catalytic activity was lost rapidly because of the degradation of the modified electrode during the electrolysis, and the grafted catalyst was slightly more stable in water than in acetonitrile.

Polypyrrole (PPy) is a conductive polymer, and PPy-containing covalently bound TEMPO was conceived as early as 1987.<sup>[18]</sup> Recently, Zhong and co-workers in China prepared a PPy TEMPO electrode (PPy-TEMPO) by the polymerisation of TEMPO-substituted pyrrole electrochemically on the surface of a Pt electrode.<sup>[19]</sup> The Pt anode is covered by a quasi-homogeneous PPy-TEMPO film (the presence of a few granules is also evident; Figure 1).

Once again, under a constant current of 20 mA cm<sup>-2</sup> with moderate stirring, the anode with a surface area of 3 cm<sup>2</sup>



**Scheme 3.** The TEMPO moiety bound to the carbon surface affords a modified electrode active towards alcohol oxidation. The stability, however, is poor. (Reproduced from Ref. [17], with kind permission.)



**Figure 1.** SEM image of the PPy-TEMPO film. Scale bar = 2.00 μm. (Reproduced from Ref. [18], with kind permission.)

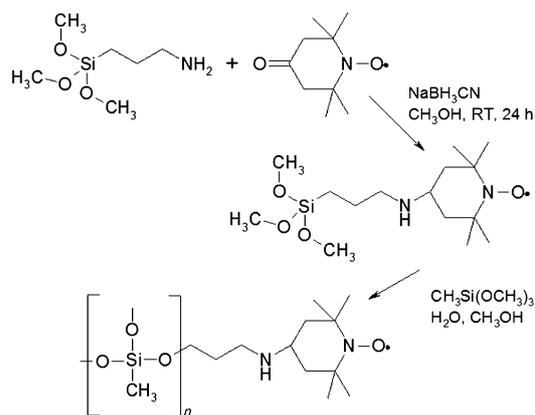
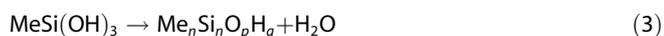
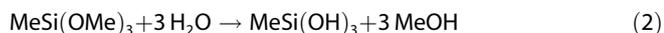
showed a high activity for the selective oxidation of benzyl alcohol (4 mmol) to benzaldehyde in NaClO<sub>4</sub>/CH<sub>3</sub>CN (0.1 M) in the presence of 2,6-lutidine as the base (20 mmol). The cathode was a Pt sheet of identical area (3 cm<sup>2</sup>). No data on the electrode stability were reported throughout the study.

### Sol-gel electrodes

As a result of their vast accessible inner porosity that allows the oxidant and reductant molecules to diffuse through the material and eventually to the surface of a conducting electrode, sol-gel electrodes, that is, electrodes modified chemically<sup>[20]</sup> using the sol-gel process, have a rich and varied electrochemistry.<sup>[21]</sup>

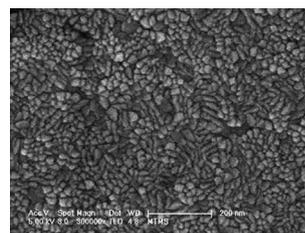
Named TEMPO@DE, the first sol-gel electrode functionalised with TEMPO was developed in 2006 (Scheme 4).<sup>[22]</sup> The active layer is made of a thin film of hydrophobic silica derivatised with TEMPO, deposited on the surface of an indium-tin-oxide (ITO) electrode, according to the general method to prepare sol-gel electrodes described by Shacham et al. in 1999.<sup>[23]</sup>

The large pH increase at the electrode surface caused by the reduction of protons near the ITO surface [Eq. (1)] catalyses the sol-gel polycondensation of methyltrimethoxysilane [MTMS; Eq. (2)] and thus ensures the electrodeposition of a thin layer of organosilica [Eq. (3)]:



**Scheme 4.** Synthesis of the TEMPO@DE electrode precursor, which is then poly-condensed electrochemically. (Reproduced from Ref. [22], with kind permission.)

If this organosilica electrodeposition is performed in the presence of aminopropyl-trimethoxysilane derivatised with the TEMPO moiety (by reductive amination with 4-oxo-TEMPO), a thin film of organosilica-entrapped TEMPO is obtained. The resulting glass surface comprises a relatively homogeneous network of densely packed organosilica particles of the size of 10–30 nm (Figure 2).<sup>[24]</sup>



**Figure 2.** SEM image of the TEMPO@DE organosilica electrode. Scale bar = 200 nm. (Reproduced from Ref. [24], with kind permission.)

The electrode showed good performance in terms of selective activity and stability in the oxidation of several primary, secondary, allylic and benzylic alcohols to the corresponding aldehydes or ketones in several consecutive reaction runs (Table 1) performed at a potential of 1.4 V (relative to the Ag/AgCl reference electrode) in the presence of 0.2 M hydrogen carbonate, which acts both as the electrolyte and as the base needed for proton abstraction in the TEMPO oxidation cycle (Scheme 1).

The potential applications of the technology come from the consideration that aromatic aldehydes such as benzaldehyde are used largely in perfume formulations as well as in cosmetic products and pharmaceuticals. Its straightforward synthesis in the aqueous phase from which the aldehyde self-separates because of its low solubility in water (0.1 g L<sup>-1</sup> at 20 °C) affords a product of high purity devoid of organic solvent and traces of transition metals.

Yields and selectivity in the conversion of benzyl alcohol were high and fully comparable to the homogeneous process

**Table 1.** Conversion of primary and secondary alcohols.<sup>[a]</sup> (Reproduced from Ref. [22], with kind permission).

Substrate	Product	Time [h]	Conversion [%]	Selectivity [%]
1-phenylethanol	acetophenone	12	98	99
benzyl alcohol	benzaldehyde	180	99	99
geraniol <sup>[b]</sup>	citral	100	85	99
cinnamyl alcohol	cinnamaldehyde	90	87	99

[a] Conditions: 0.5 mmol alcohol, TEMPO@DE (1 cm<sup>2</sup>), water (10 mL), NaHCO<sub>3</sub> (0.2 M). Conversion and selectivity determined by GC. [b] Reaction in H<sub>2</sub>O/CH<sub>3</sub>CN (7:3). The oxidation of alcohols (0.5 mmol) was performed in 10 mL of buffered water (0.2 M in NaHCO<sub>3</sub>), although for alcohols with low water solubility (geraniol, for instance) a CH<sub>3</sub>CN/H<sub>2</sub>O solution 30:70 (v/v) was employed. Initial substrate concentration was 0.05 M. For all the substrates, the selected potential was 1.4 V and the electrolysis was performed under fast stirring (900 rpm).

using NaOCl as the primary oxidant. The electrode was remarkably stable, even though the reaction was slow.

To advance this approach, most recently Karimi and co-workers described the first electrode surface functionalised with a thin layer of ordered mesoporous silica doped with TEMPO.<sup>[13]</sup>

In detail, with the aim to obtain a sol-gel electrode with superior diffusion properties, the team used the electro-assisted self-assembly (EASA) process introduced in 2007 by Walcarius and co-workers<sup>[25]</sup> to form an ordered MCM-41 mesoporous silica film that consists of hexagonally packed channels perpendicular to the electrode surface. The silica channels were thus functionalised with aminopropyl residues followed by reductive amination with 4-oxo-TEMPO.<sup>[13]</sup>

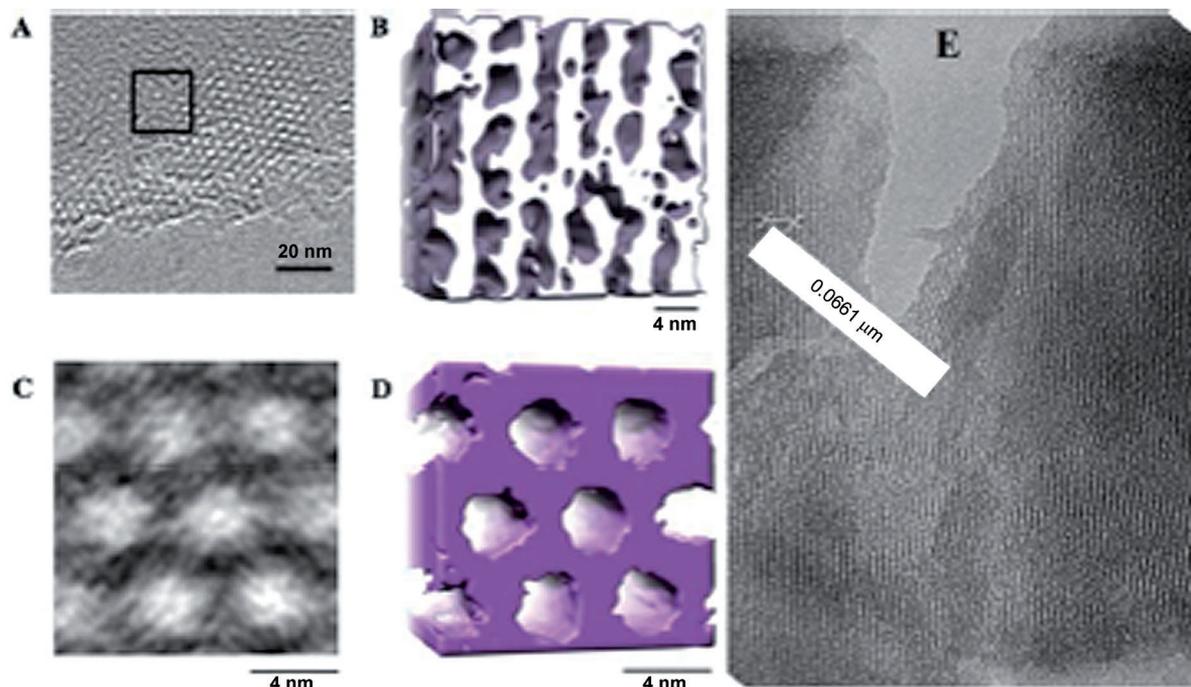
Structural investigation of the film at the surface of the TEMPO-grafted mesoporous silica electrode (TGSE) revealed

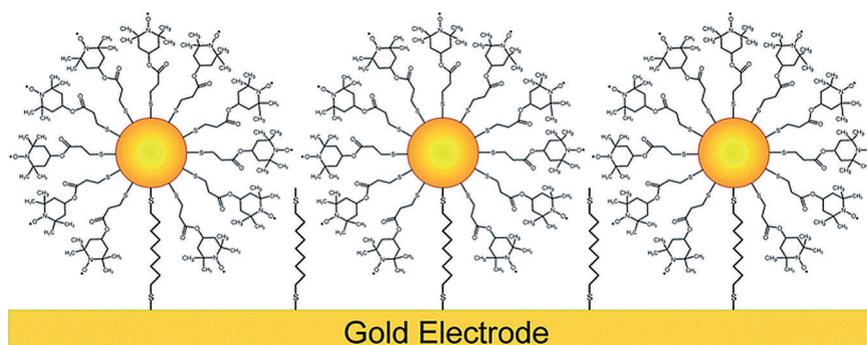
highly porous, well-defined, 2D hexagonal mesostructures perpendicular to the electrode surface (Figure 3).

Tested extensively on a 20 mmol scale, the resulting electrode is the most active TEMPO-based alcohol oxidation catalyst ever reported. Suggested to be the result of the lack of restriction constraints because of the ordered channels of the MCM-41, the trend in turnover frequency (TOF) values was identical to that of homogeneous TEMPO-mediated oxidations discussed by De Nooy et al.<sup>[11]</sup> The TEMPO-functionalised ordered mesoporous silica electrode showed a higher efficiency toward the oxidation of primary alcohols, in particular for benzylic and allylic substrates, followed by aliphatic alcohols.

### Nanostructured Au electrodes functionalised with TEMPO

An interesting, completely new approach was reported recently by Megiel and co-workers, who functionalised a Au electrode with TEMPO-coated Au nanoparticles (NPs).<sup>[26]</sup> In detail, Au NPs covered by TEMPO derivatives with a well-defined coverage and narrow size distribution were first synthesised in one step by the mild reduction of a solution of HAuCl<sub>4</sub> with NaBH<sub>4</sub> in the presence of bis[2-(4-oxy-2,2,6,6-tetramethylpiperidine 1-oxyl)ethyl] disulfide (DiSS). Then the Au/TEMPO NPs were bound to the surface of a Au disc electrode derivatised previously with a 1,9-nonanedithiol linker by simply stirring the functionalised electrode in an acetone solution of TEMPO NPs (1 mg mL<sup>-1</sup>) overnight. The idealised structure of the resulting electrode is shown in Figure 4.

**Figure 3.** TEM images (A, C, E) and reconstructed images (B, D) of the TGSE electrode. (Reproduced from Ref. [13], with kind permission.)



**Figure 4.** Representation of a Au electrode functionalised with TEMPO/Au NPs. (Reproduced from Ref. [26], with kind permission.)

The team also functionalised the electrode surface with a monolayer of TEMPO DISS derivative. Tested in benzyl alcohol oxidation, the resulting closely packed monolayer-covered TEMPO-SH electrode, however, showed 20 times lower catalytic current compared with the NP-covered electrode, which is in full agreement with the much larger peak current that corresponds to TEMPO oxidation in the latter electrode and reflects both the increased number of catalytic sites available for the same geometric area and the better accessibility of the TEMPO groups attached to the Au NPs.

Self-assembled monolayers (SAMs) on Au electrodes are costly because of expensive Au but they are already in use in industry for a variety of chemical purposes because of their great stability.<sup>[27]</sup> In addition, the electrochemical response at each of the modified Au electrodes was practically constant after 15 voltammetric cycles (the difference between the anodic peak current of 1st and 15th voltammograms was less than 8%).

### Accessibility and stability

As with the related electrocatalytic oxidation of benzyl alcohol mediated by SAMs derivatised with TEMPO deposited on Au,<sup>[28]</sup> the electrocatalytic performance is governed by the physical accessibility of the heterogenised nitroxyl radicals by the alcohol molecules in solution and by the regeneration of the catalytic radicals through the comproportionation of oxoammonium and hydroxylamine before electrochemical re-oxidation.

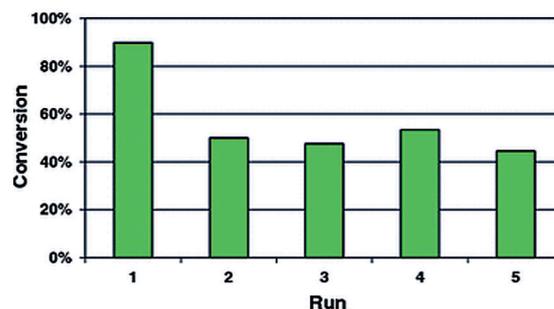
Several aspects, however, are unique to the 3D sol-gel encapsulation within silica or organosilica cages<sup>[29]</sup> compared to the 2D surface derivatisation of organic polymers. First, once encapsulated, the nitroxyl radical moieties bound at the cage surface are isolated reciprocally and available for the faster and easier electron transfer from the TEMPO moiety to the electrode surface. Indeed, the encapsulation of the TEMPO moiety in the TEMPO@DE organosilica pores results in the alteration of the electrochemistry of the dopant TEMPO molecule, which has an oxidation potential at approximately 0.7 V (vs. Ag/AgCl) in solution, and upon entrapment shows a relatively high current that occurs already at 0.2 V.

Second, the sol-gel encapsulation in the inner pores of the organically modified silica (ORMOSIL) cages protects the radi-

cals from chemical degradation caused by 1) the intermolecular quenching of the radicals tethered at the surface (through oxoammonium ion mediated cleavage of amino bonds)<sup>[30]</sup> and 2) the action of the hydroxide ion (at pH > 13) to afford a hydroxylated oxoammonium species, which in turn undergoes further anodic oxidation with the irreversible loss of TEMPO.<sup>[31]</sup>

Finally, the organosilica electrode is highly hydrophobic and shows a pronounced low degree of hydrophilicity as a result of the depletion of silanol groups at the organosilica matrix surface.<sup>[32]</sup> This prevents silica dissolution in the alkaline environment, which is the main chemical weakness of silica-based materials.

As a result, the same catalytic TEMPO@DE electrode could be used in tens of consecutive experiments with different substrates without any treatment between consecutive oxidative runs besides sonication in distilled water.<sup>[22]</sup> After an initial decay of the activity likely caused by the deactivation of the radicals at the outer surface of the organosilica mesopores, the catalytic activity remains practically constant for numerous, consecutive reaction runs (Figure 5).



**Figure 5.** Conversion of 1-phenylethanol to acetophenone mediated by the organosilica electrode TEMPO@DE after 15 h (1.4 V). (Reproduced from Ref. [22], with kind permission.)

The main limitation of the TEMPO@DE electrocatalytic electrode is the low reaction rate, which however, is mainly because of the poor beaker cell configuration employed to demonstrate the proof-of-concept of a sol-gel-hydrophobised TEMPO-based electrode. The electrode indeed has a large inner mesoporosity, which favours the diffusion of reactants and products to and from the encapsulated TEMPO moieties.

Indeed, to improve mass transfer in solution with the TGSE electrode and to produce an ordered mesoporous TGSE electrode with easily accessible meso-channels perpendicular to the electrode surface, Karimi and co-workers improved the electrochemical cell by employing additional graphite plates in a large-diameter hollow tube and adding steel plates between the graphite electrodes, which thereby increases the overall electrode functional surface up to 260 cm<sup>2</sup>.<sup>[13]</sup>

Run	Conversion [%]	Time [min]
1	100	100
2	100	125
3	95	158
4	95	200
5	95	240

[a] Reaction conditions: benzyl alcohol (1 mmol), water (100 mL), NaHCO<sub>3</sub> (10 mmol), Na<sub>2</sub>CO<sub>3</sub> (1 mmol),  $E = 1.0$  V vs. Ag/AgCl.

Alas, the purely inorganic nature of the MCM-41 silica is responsible for the rapid degradation of the TGSE electrode (Table 2). Hence, although 100 min was enough to convert benzyl alcohols into benzaldehyde fully, after another four runs, the time more than doubled to 240 min with a maximum yield of 95%.

Such limited stability is most likely because of the chemical instability in the buffered alkaline solution (pH 9) in which the reaction is performed. This is in agreement with the poor stability of an amorphous, entirely inorganic SiO<sub>2</sub> electrode functionalised with TEMPO, which, employed at pH 9.3 in the electro-oxidation of benzyl alcohol, lost its activity entirely after only two runs.<sup>[24]</sup>

## Conclusion and Outlook

The successful development of electrodes functionalised with 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) in industrial processes would develop a new class of clean technologies for the waste-free production of a variety of specialty chemicals, which use electrons and alcohols as the only reactants.

As emphasised by Brown,<sup>[33]</sup> the progress of clean synthetic procedures driven by an electrical current has often been hindered by the lack of user-friendly electrolytic equipment. In cooperation with the pharmaceutical industry, Brown's team has advanced the homogeneous TEMPO-mediated alcohol oxidation route so that it can now be performed continuously at ambient temperatures without added electrolyte in a micro-flow electrolysis cell that fits into a commercial micro-flow reactor.<sup>[34]</sup>

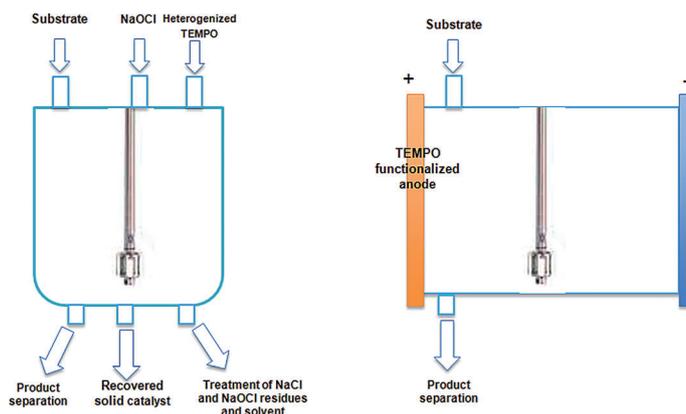
Furthermore, Pletcher suggested that the lack of adoption of organic electro-synthesis is primarily because of the general use of beaker cells,<sup>[35]</sup> the inherently poor design and mass transport regime of which is suited only for reactions that afford 100 mg of product. Finally, the prolonged utilisation of obsolete (costly) Pt and (toxic) Hg electrodes has largely limited industrial and academic interest.

For at least a decade, this situation has been evolving rapidly as it is now realised clearly, to paraphrase Little et al.,<sup>[5]</sup> that a selective oxidation electrochemical process, using electrons as the simplest and cleanest redox reactants, would simply afford no waste, which is even better than heterogene-

ous catalysis over recyclable solid TEMPO-based catalysts (Figure 6).

As a result of a number of unique advantages, the homogeneous and heterogeneous TEMPO-mediated oxidation of alcohols has been widely and increasingly adopted in industry.<sup>[7]</sup> The development of an efficient, stable electrode for the heterogeneously catalysed electro-oxidation of alcohols based on TEMPO redox chemistry is highly desirable.

Besides process efficiency (high yield, selectivity and lack of waste), the main factor that guides the adoption of the technology will be the ongoing cost of the production of carbonyls



**Figure 6.** Comparison between a conventional TEMPO-mediated oxidation process catalysed heterogeneously (left) and the corresponding electrochemical process (right). (Adapted from Ref. [5], with kind permission.)

by electro-oxidation. Unstable electrodes, though initially very active, will not find practical application.

In conclusion, we argue that organosilica-based sol-gel-derived electrodes, are likely to find practical use soon as they offer the required long-term stability along with three major advantages:<sup>[21]</sup> 1) the ease with which electrodes of the most disparate shape, size and composition can be functionalised reproducibly, 2) the possibility to miniaturise the electrode and 3) the unique porous structure permeable to external reactants that can penetrate into the thin film and react with high selectivity.

The achievements in the chemical research discussed critically in this account will hopefully provide guidance for the development of electrodes functionalised with the organocatalyst TEMPO for the entirely waste-free synthesis of valuable carbonyl compounds from different alcohols.

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**Keywords:** alcohols · electrochemistry · organocatalysis · oxidation · waste prevention

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