



o-Toluidine in electrochemistry – an overview

Elisabeth Weber¹ · Elmar Richter¹ · Rudolf Holze^{2,3,4}

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Abstract

The substituted aromatic amine *o*-toluidine (2-methylaniline, 1-amino-2-methylbenzene) is frequently encountered in electrochemical research as a soluble corrosion inhibitor dissolved in aqueous media used e.g., in cooling systems, as a homomonomer for formation of intrinsically conducting poly-*o*-toluidine and as a comonomer in formation of respective copolymers and their composites. The obtained polymers are suggested as corrosion protection coatings, as active materials in devices for electrochemical energy storage, but more frequently, they are examined as active components in electrochemical sensors. The significant and pronounced carcinogenicity of *o*-toluidine has hardly been addressed; presumably, most researchers are not even aware of this property. After a brief summary of the health risks and effects, the following overview presents typical examples of said studies and applications. If possible, substitutes with lower health risks are proposed, at least further studies enabling such replacement are suggested.

Keywords *o*-Toluidine · 2-Methylaniline · Corrosion inhibition · Corrosion protection · Intrinsically conducting polymers · Copolymers · Electrochemical sensors · Carcinogenicity

Introduction

o-Toluidine (Fig. 1) is frequently encountered in electrochemistry.

Since the discovery of intrinsically conducting polymers (ICPs [1]), numerous studies dealing with their formation, characterization, electrochemical modification, and their possible applications have been published. One family of monomers particularly extensively studied starts with aniline

and its substituted relatives. This popularity is presumably related to the possibility, that most of the compounds can be electropolymerized from acidic aqueous electrolyte solutions, this also applies to copolymers [2] using *o*-toluidine as one comonomer. Applications range from the use in supercapacitors, sensors to protective coatings covered in detail below. General overviews on ICPs and their applications in particular in sensors are available [3–9]. The use of *o*-toluidine as dissolved corrosion inhibitor is presumably suggested because of the various modes of interaction between this molecule and a metallic surface necessary to inhibit either the cathodic dioxygen reduction (in case of corrosion at air) or reduction of protons (corrosion in acidic environments) and/or the anodic metal dissolution.

The pronounced carcinogenicity of *o*-toluidine has been reported [10, 11] but, apparently, hardly been recognized (and practically never mentioned, see [Supplementary](#)

This work is dedicated to the memory of Wolf Vielstich whose numerous contributions to electrochemistry and heterogeneous catalysis have advanced electrochemistry during his long scientific career.

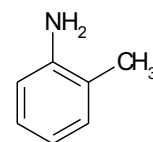
✉ Rudolf Holze
Rudolf.holze@chemie.tu-chemnitz.de

¹ Institute for Cardiovascular Prevention, Ludwig Maximilians University, Pettenkoferstr. 9, Munich 80336, Germany

² State Key Laboratory of Materials-Oriented Chemical Engineering, School of Energy Science and Engineering, Nanjing Tech University, Nanjing, Jiangsu Province 211816, China

³ Institute of Chemistry, Saint Petersburg State University, St. Petersburg 199034, Russia

⁴ Institute for Chemistry, University of Technology, Straße der Nationen 62, Chemnitz 09111, Germany



o-toluidine; 2-methylaniline

Fig. 1 Structural formula of *o*-toluidine

Materials listing of all examined publications) by most researchers in electrochemistry and corrosion protection. This report provides first an overview on the carcinogenicity of *o*-toluidine and associated health risks, discusses representative electrochemical studies, and suggests possibilities to avoid this risk by e.g., using other compounds or at least *m*- or *p*-toluidine. It is focused on electrochemical studies wherein either *o*-toluidine is used as such (inhibitor) or as starting material (for a coating, a copolymer, a sensor) or is present in a product relevant to electrochemistry. There are numerous reports dealing with behavior and properties of *o*-toluidine, its polymers, copolymers, and composites in many fields of science (see e.g., [12–14]); these reports are not included here. Neither included are fundamental electrochemical and spectroelectrochemical studies of POT and its copolymers (see e.g., [15]).

Toxicology and health risks of *o*-toluidine

Commercial use of *o*-toluidine started in the 2nd half of the nineteenth century with the invention of the first synthetic organic dyes mauveine and fuchsine/magenta [10]. *o*-Toluidine is a major component of these so-called aniline dyes, which are still in use [16]. A high incidence of occupational bladder tumors in fuchsine workers was reported by Rehn in 1895, who wrongly blamed aniline as the responsible agent [17]. Minor impurities of other arylamines, 2-naphthylamine and 4-aminobiphenyl, rather than *o*-toluidine have been made responsible for the extremely high incidence of bladder cancer observed in fuchsine production. Bladder cancer in the rubber industry where other arylamines did not play a role [18] finally led to the classification of *o*-toluidine as a proven human bladder carcinogen, first in 2006, by the German MAK commission [19, 20], and in 2010, by the International Agency for Research on Cancer (IARC [16]). Nonetheless, *o*-toluidine is up to now quite differently regulated e.g., in the European Union. Under the aspect of consumer protection, the use of azo dyes in textiles and leather that may cleave carcinogenic arylamines including *o*-toluidine were completely banned in 1994 in Germany [21] and accordingly regulated in 1999 by the EU [22]. However, EU did not follow the classification of *o*-toluidine as a proven human carcinogen but put it only in category 1B “known or presumed to have carcinogenic potential for humans based primarily on animal evidence” [23] and defined a limit of exposure of 100 ppb for an 8 h work shift [24]. However, based on a cohort of 1875 workers manufacturing chemicals used in the rubber industry and employed any time during 1946–2006, exposure to 1 ppb of *o*-toluidine already gives a 1–7 per thousand excess lifetime risk of bladder cancer [25].

Perhaps, risks of exposure when handling the *o*-toluidine in the lab and during possible manufacturing as well as when

dealing with polymers, possibly remaining residual monomers, should be addressed and alternatives to this arylamine should be used, whenever possible.

o-Toluidine as dissolved corrosion inhibitor

Attempts and methods to meet the huge challenges placed by corrosion of all forms, but particularly of metals, by corrosion protection are numerous and well-developed into many different approaches as described in several monographs [26–38]. Depending on the details of the material or system needing protection, corrosion inhibitors may be a practically relevant or even attractive option. For systems with large amounts of circulating water as a heat transfer medium (power stations, air-conditioners, heat-exchangers), dissolved inhibitors added to the circulating medium at concentrations as small as possible can slow down the metal dissolution (anodic protection) or the hydrogen evolution/dioxygen reduction (cathodic protection). In descaling and cleaning processes with pickling solutions, carbonate deposits resulting from water hardness and layers formed during exposure of a metallic object to the environment (superficial corrosion products) are removed by exposing the object to suitable, frequently highly acidic, and chemically aggressive solutions. Removal of oxide coatings formed during exposure of a metal to air is another task of chemically aggressive pickling solutions (see e.g. [39]). Beyond dissolution of the unwanted coatings, corrosion of the metal under the deposit may occur but should be avoided by suitable inhibitors. Possible inhibitors must be sufficiently soluble in the circulating medium (water); they should be economically viable, must have sufficient chemical stability under operating conditions (i.e., at elevated temperatures), and must be environmentally compatible. This obviously includes a toxicity as low as possible. For the latter reason, “green inhibitors” obtained from natural sources (plants) have attracted growing attention in recent years; their natural origin is assumed to be an indicator of inherent environmental compatibility.

Inhibitors, whether synthetic or of green origin, mostly act by adsorptive interaction with the surface to be protected [40]. Such interaction is supported by functional groups in particular with heteroatoms (amino groups, sulfur-containing groups) and by structural specifics like double or triple bonds or aromatic ring systems [41–43] or pronounced polarity of a potential inhibitor molecule [44]. Such adsorption can be verified in many cases by spectroscopic methods [45]. Polarity of the inhibitor molecules is a property of particular importance for adsorption as pointed out in [46] and discussed in detail in corrosion studies earlier [41, 44]. Further orientation about the strength of adsorptive

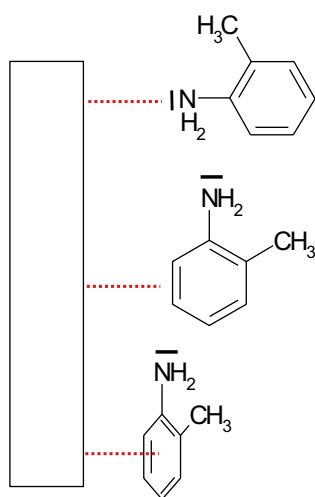


Fig. 2 Conceivable modes of inhibitor-surface interactions with unprotonated *o*-toluidine

interaction may be obtained from thermodynamic adsorption studies, results have been tabulated [47]. According to the rich published literature, selection of candidate materials nevertheless seems to be based mostly on trial and error; experience may help too. Substituted aromatic molecules are particularly attractive candidates because they contain several potential anchoring sites for adsorptive interaction: The substituent(s), the aromatic π -system, and the hydrogen atoms are at the ring system. As shown in Fig. 2, for the case of unprotonated *o*-toluidine (i.e., in neutral corrosive environments), various arrangements are conceivable. In acidic solutions, protonation of the amino nitrogen may change the options.

This general observation [48] has been discussed in detail in reports on studies of adsorption of aromatic molecules using surface-enhanced Raman spectroscopy (see e.g. [46] and references therein). NMR spectroscopy has been employed to understand the wide variation of corrosion efficiencies of aromatic compounds [49]. A correlation between the chemical shift of the signal attributed to the amine proton and inhibition efficiency was noted. This empirical approach may help in assessing inhibitors. Inhibition of carbon steel corrosion in contact with an aqueous solution of sulfuric acid by *o*-toluidine has been studied; inhibition efficiencies around 86% at millimolar inhibitor concentration were observed based in good agreement on weight loss, impedance, and potential polarization measurements [50]. Various *o*-substituted anilines have been tested as corrosion inhibitors for steel in aqueous sulphuric acid solution with *o*-toluidine showing the lowest efficiency [51]. A second mode of operation of a dissolved inhibitor is formation of an insoluble protective layer on the metal surface. Such layer acts as a barrier like the coatings discussed in a later section.

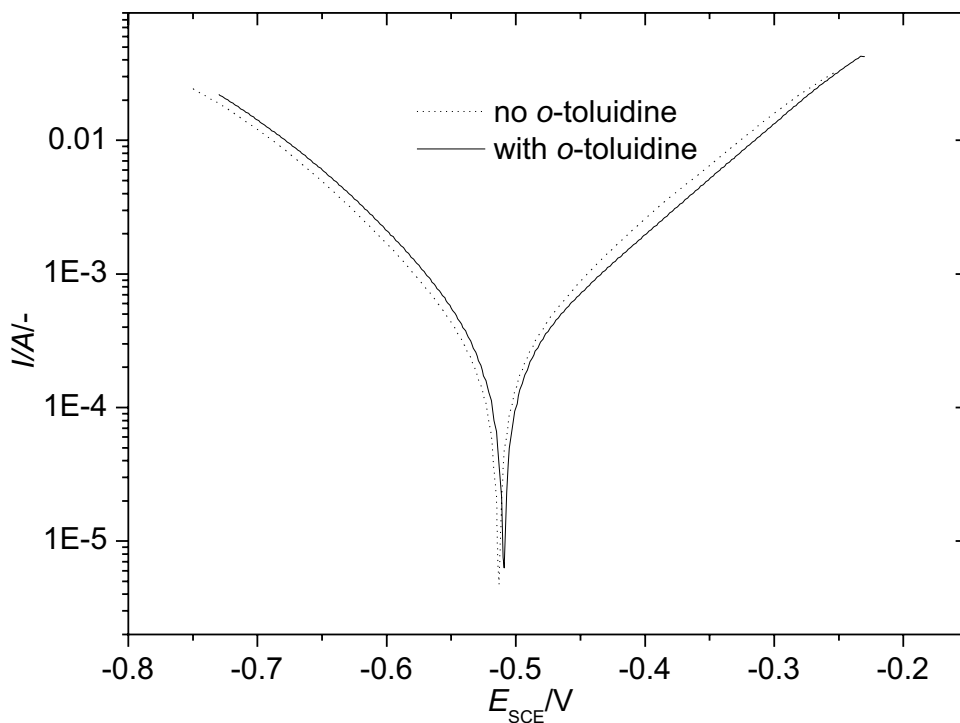
In a broader study of the inhibition, efficiency of numerous substituted aromatic molecules against corrosion of mild steel 1020 exposed to hydrochloric acid including theoretical considerations *o*-toluidine showed only rather poor performance [41]. This observation is at variance with a much wider study of aromatic inhibitors for the same corroding system [52] wherein *o*-toluidine showed a fairly good performance. A possible way to improved performance has been suggested: mixtures of two inhibitors showed much higher protection efficiencies without needing *o*-toluidine. In a comparison of the corrosion, inhibition of mild steel in aqueous sulfuric acid by selected nitrogenous aromatic compounds *o*-toluidine showed the poorest performance [53].

Babu and Holze have compared the inhibition efficiency of several *o*-, *m*-, and *p*-disubstituted anilines including *o*-toluidine [54]. *o*-Phenylenediamine turned out to be the most efficient; this can be taken as an example for a critical examination of the real need to use *o*-toluidine and to replace it with a less toxic and even more efficient molecule. The minor limitation of this report – only one electrochemical method has been used in addition to hydrogen permeation studies – has been amended in a more recent report [55] wherein three standard electrochemical methods have been used confirming the conclusion of the earlier report.

Corrosion inhibition activity of a Schiff base ligand prepared from *o*-toluidine and *o*-chlorobenzaldehyde in contact with mild steel showed a significant dependency on inhibitor concentration ranging from 47% at 20 ppm to 90% at 90 ppm inhibitor [56]. Similar results were obtained with further Schiff bases [57, 58]. Adducts formed from sunflower fatty acids and various substituted anilines have been tested as efficiency-enhancing additives in varnishes [59]. *o*-Toluidine showed lower efficiency than *m*- and *p*-toluidine. A typical result is shown in Fig. 3.

Most studies deal with corrosion of steel. Less frequently inhibiting action with brass, zinc, and other commonly used metals and their alloys has been examined. The inhibition efficiency of various aromatic amines on 70/30 brass in contact with aqueous nitric acid has been investigated [60, 61]. Possibly related to a chemical reaction (diazotization) of anilines with nitric acid *o*-toluidine has turned out to perform poorly only in this system. In a similar study with brass 63Cu–37Zn with various aromatic amines as corrosion inhibitors the effect of *o*-toluidine depended significantly on the concentration of nitric acid as the corrosive medium, its performance varied from poorest to best without any apparent explanation [62]. Copper corrosion is relevant in e.g., descaling and cleaning processes with pickling solutions. Some *o*-substituted anilines including *o*-toluidine have been examined [63]. *o*-Toluidine showed only moderate efficiency. Corrosion inhibition for zinc exposed to diluted hydrochloric acid by various aromatic amines has been studied; *o*-toluidine showed only moderate efficiency [64].

Fig. 3 Potentiodynamic polarization curves for a mild steel C15 sample in 1 M HCl solution without/with inhibitor 6 mM *o*-toluidine (further details see [55])



Corrosion protection for Al-2S alloy in aqueous HCl solution by various aliphatic and aromatic amines has been examined in a comparative study [65]. *o*-Toluidine showed high efficiency very close to the value for *o*-chloroaniline. At high inhibitor concentration, *m*-toluidine performed as good as the *o*-compound. With Al-3S alloy exposed to trichloroacetic acid plain aniline performed better than the toluidines [66]. In an even wider study, numerous amines as possible inhibitors for corrosion of various aluminum alloys have been tested [67]. *o*-Toluidine showed significant efficiency, better than *m*-toluidine. This was noticed as confirmation of earlier observations by Hackerman and Makrides [44] suggesting the superior performance of *o*- and *p*-substituted compounds because of associated structure-induced electronic effects. Some aniline derivatives have been studied as corrosion inhibitors for aluminum 57S alloy exposed to hydrochloric acid of various concentrations; *o*-toluidine showed the lowest protection [68]. *o*-Toluidine applied as corrosion inhibitor for aluminum-magnesium alloy exposed to phosphoric acid showed only mediocre efficiency [69]. The authors of this comparative study of a wide selection of aniline and substituted anilines highlight the adsorptive interaction of the inhibitor molecule with the metal surface via the nitrogen atom (presumably its lone electron pair in particular as stressed elsewhere based on spectroscopic evidence [70, 71]) and/or the aromatic π -electron system as also mentioned above. Several aromatic inhibitors including various substituted anilines have been used as corrosion inhibitors for B26S

aluminum–copper alloy in contact with aqueous phosphoric acid [72]. Most effective was *p*-toluidine, aniline was less effective, *o*-toluidine even less. In a similar study, protection afforded by toluidines to aluminum–copper alloy in contact with aqueous hydrochloric acid was examined [73]. The sequence of efficiencies of the toluidines already observed with phosphoric acid was found again.

A very specific application of organic corrosion inhibitors is their use as “volatile inhibitors” which are e.g., sprayed on metal products for temporary corrosion protection during transport or short-term storage or may be evaporated in the storage room [74]. This use adds one more requirement regarding the properties of the inhibitor: sufficient vapor pressure at moderate, practically applicable temperatures which enables transport of the inhibitor to the surface to be protected, where it will be adsorbed finally.

The rather limited use of theoretical tools in understanding corrosion processes, in particular, corrosion inhibition by molecular inhibitors, has been deplored before. The inadequate combination with in situ-spectroscopic methods possibly helpful in verifying both theoretical models and conclusion from experimental observations is one more approach meriting bigger attention. A study of the inhibitor action of aniline and its substituted relatives has been reported [75]. According to the theoretical findings, para-substituted anilines should be more effective than ortho-substituted. Extended Hückel molecular orbital calculations performed with some aliphatic amines yielded correlations between calculated molecular properties (charge density

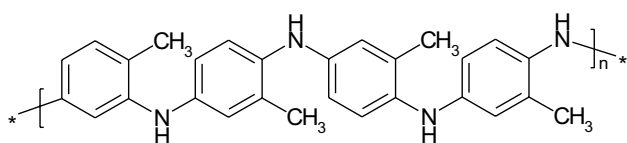


Fig. 4 Simplified schematic structure of POT

on nitrogen atom, E_{HOMO}) and observed corrosion rates possibly helpful in selecting inhibitors [76]; the particular importance of charge density on the nitrogen atom and its correlation with inhibition efficiency has been observed also with *N*-heterocyclic amines and their derivatives [77].

Poly-*o*-toluidine and copolymers with *o*-toluidine and their applications

Poly-*o*-toluidine (POT, Fig. 4) and its copolymers can be prepared by electropolymerization and by oxidative chemical polymerization.

The effect of the methyl-substituent on polymerization rate and product properties for various substitution pattern has been studied [78]. In the former procedure, the obtained material is deposited as a film on the substrate that also acts as the electrode. In many applications, this approach is efficient for various reasons. The obtained polymer will stick most likely on the substrate well enough for most applications. It is deposited only on the substrate; except for possibly soluble oligomers formed in the polymerization reaction, which may diffuse away before being deposited, no significant losses can be expected. Statements made in passing in a few cases seem to indicate that coatings of POT tend to be more stable, better adhering, and denser than those of PANI. Concerns regarding energy expenses are hardly relevant. The low total amounts of ICP formed in an electrochemical reactor (deposition cell) by a heterogeneous process may pose a problem when attempting to prepare large amounts. Except for uses (like in battery electrodes) where substantial amounts of the ICP are required this limitation appears to be minor.

Chemical polymerization results in powdery materials. Depending on the intended use, the poor tractability, in particular very small solubility in most common solvents, is a major obstacle. Various approaches have been tried; the use of oligomers instead of polymers is one option. Another one leading directly to POT is the use of substituted anilines as a starting material resulting in slightly more soluble ICPs [79]. The increased solubility afforded by *o*-substitution like in *o*-toluidine has been ascribed to a changed torsional angle between adjacent repeat units [80]. Unfortunately, other properties like electronic conductivity, extent of electronic conjugation, or speed of charge carrier transport change to

the worse [81]. A further pathway to more soluble ICPs is the formation of copolymers; for typical examples, see [82, 83]. Alternative polymerization protocols yielding soluble or at least better tractable ICPs may help to avoid the use of critical monomers [84, 85].

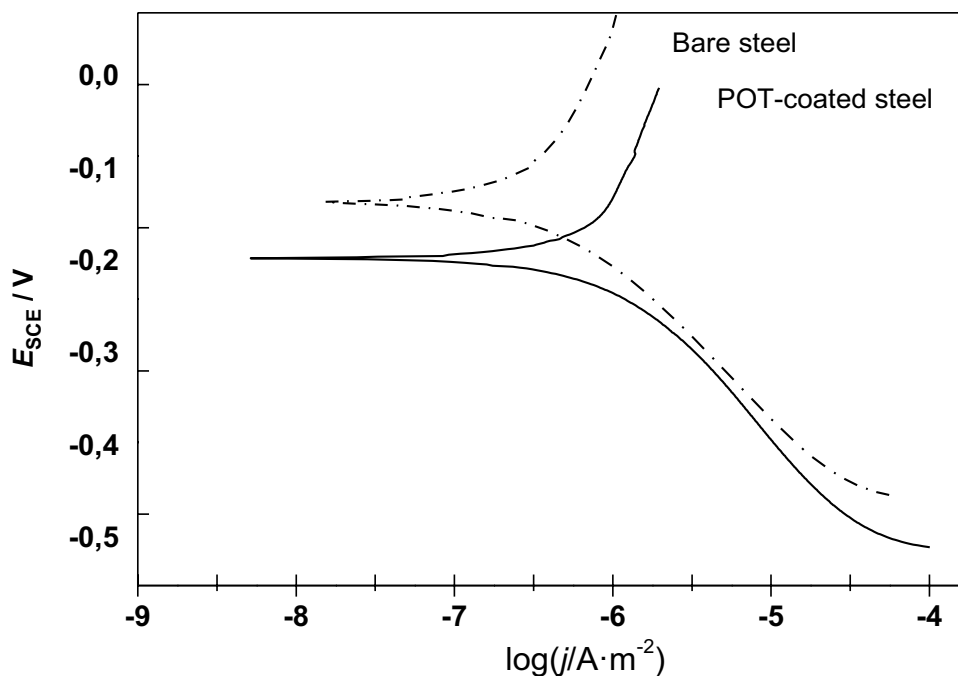
Following ICPs with *o*-toluidine prepared and examined for a particular function are discussed because the authors wish to draw attention of both researchers and users to the inherent risks of using this material in particular when attempted on a larger scale. The numerous studies of POT formation and characterization (for examples, see [86–88]) are not reviewed because a broader risk associated with use of *o*-toluidine on a technical scale appears to be unlikely.

Application as coating for corrosion protection

Corrosion of metals can be suppressed or at least slowed down by a wide variety of practical approaches (see preceding section). Coatings (barrier layers) with paints or polymers inhibiting access of dioxygen as the most frequently encountered cathodic reactant as well as water and electrolytes (i.e., salts) are among these options. Very early after the discovery of electrochemically active ICPs, their use as protective coatings has been suggested [89]. Beyond the mechanical barrier effect, which is not always as good with ICPs because of their sometimes porous morphology, other electrochemical effects are observed [90]. Utilizing the electrochemical activity of ICPs, the electrode potential of the metal to be protected is shifted into a direction where corrosion is less likely. The redox potential at which redox transformation of an ICP happens depends on various properties, changing substituents at the starting monomer is one option. Systematic studies of such substituent effects have been reported; for an example, see [91–93]. Another option of modification of this redox potential is formation of a copolymer [2]. A further advantage becomes effective when the coating is damaged. The potential-control afforded by the ICP keeps even the exposed metal surface in a stable state.

Coatings can be applied by electropolymerization. Anodic oxidation, i.e., corrosion, of the metal to be protected may limit this approach. A further option is chemical polymerization in a solution of the monomer with the items to be coated using chemical oxidants. The yield of the process and adherence of the coating may be insufficient. Finally, attempts have been reported to prepare soluble forms of ICPs; for examples, see [79, 84, 85, 94–96]. In addition to POT, copolymers have been suggested. Further reasons for using copolymers have been reviewed elsewhere [2]. In addition to the use of an ICP as a plain coating, the use of ICPs in composite coating has been examined. The function of

Fig. 5 Potentiodynamic polarization curves for (a) stainless steel and (b) POT-coated steel in an aqueous 3% NaCl solution (for further details, see [79])



the “other” constituent, which frequently is the major fraction, varies and will be addressed when considering reported examples below.

POT deposited at various current densities on stainless steel brought finally into contact with seawater showed best corrosion protection when deposited at a lowest current density [97]. Deposition times were the same for all tests. Accordingly, the presumably thinnest coating performed best, and low porosity agrees with this observation. Because low current density implies lower electrode potential and accordingly less overoxidation and a more dense coating because of a lower rate of deposition nuclei this conclusion agrees with earlier observations. No evidence was provided regarding the obvious question of whether plain PANI would show similar behavior. The addition of lanthanum and zinc ions improved protection efficiency of POT coatings from 82.8% to about 98%; unfortunately, the actual mode of operation remains clouded in the report [98]. An attempt to establish POT as a coating alternative to PANI (see [99]) on low carbon steel has been reported [100]; unfortunately, the obtained improvement (50% reduction of corrosion rate) was not verified. Deposition of POT films on stainless steel from an aqueous solution of sodium salicylate provided a reduction of the corrosion current to 1/45 of its initial value without coating [101]. A similar efficiency was observed with POT coated from an aqueous tartrate-based electrolyte solution [102]. Corrosion protection of steel afforded by poly(*N*-methyl pyrrole) and its copolymer with *o*-toluidine has been compared, the homopolymers turned out to be more efficient [103].

Solubility of POT obtained via inverse emulsion polymerization was the reason of using *o*-toluidine, the coating on steel provided 77% protection efficiency [79] (Fig. 5).

From aqueous solutions of oxalic acid, POT could not be deposited as coherent and stable films on mild steel [104]. Instead, the authors tried copolymers with pyrrole at various comonomer feed ratios. Reasons for selection of *o*-toluidine were not provided, and based on impedance measurements, inhibition efficiencies > 90% somewhat depending on the comonomer ratio were observed. Such soluble copolymer was prepared by chemical polymerization; a coating on carbon steel was subsequently applied with a saturated solution of the dissolved copolymer in *N*-methyl-2-pyrrolidone¹ NMP [105]. Protection of up to 99.99% was reported; specific reasons for the use of *o*-toluidine were not provided. Possibly increased solubility induced by the latter was a reason. These authors later compared efficiency of this copolymer with one obtained with aniline [106]. The latter one performed better. A ternary polymer of pyrrole, *o*-anisidine, and *o*-toluidine has been tested; protection efficiencies reached 95.3% only [107]. A copolymer of *o*-toluidine and aniline soluble in NMP was prepared by chemical polymerization and subsequently applied to mild steel samples [108]. Various corrosive environments were examined; in most cases, the copolymer performed best with protection efficiencies above 93%. Although not clearly addressed higher solubility of the ICP induced by *o*-toluidine was the main reason to use it. A form of POT soluble in several organic solvents

¹ To call this procedure chemical deposition is misleading at best.

has been reported [109]. Its corrosion protection afforded to stainless steel in contact with aqueous 3.5% NaCl solution was tested; a protection efficiency of 56% was noted.

On iron surfaces, polymers of several ring-substituted polyanilines (PANI) could be obtained by electropolymerization from aqueous oxalic acid solutions [110]; they afforded less protection than simple PANI. On copper, an adhering layer of POT could be formed from an aqueous solution of sodium oxalate with the monomer [111]. Rate of corrosion was reduced to 1/40; the suggested general improvements of a polymer afforded by substituents at the polymer skeleton are not revealed. In a related study of the same system, it was observed, that POT took place on a copper surface passivated with copper oxalate [112]. Coatings of POT from these oxalate-based electrolyte solutions on steel were also obtained; their protective capabilities were not explored [113]. Poly(*o*-anisidine-co-*o*-toluidine) electrochemically coated on copper from an aqueous solution of sodium salicylate provided slightly higher protection efficiencies than the respective homopolymers [114]. In a comparative study, protection efficiencies of PANI, POT, and the respective copolymer applied by electropolymerization to stainless steel were examined; *o*-toluidine did not provide any advantage [115]. In a similar study, the same comparison was performed (although the terms composite and copolymer somehow got mixed up) [116]. Although the reported corrosion current with a coating of POT was smaller by two orders of magnitude, the authors concluded that the composite (possibly copolymer) film afforded the best protection. POT could be electrodeposited from a salicylate-based electrolyte solution on brass; the corrosion rate in aqueous 3% NaCl solution dropped by a factor of 1/800 with an 8- μm -thick coating [117]. Although some hardly relevant reasons for using *o*-toluidine were provided, possibly, the advantages of its use highlighted above were in effect.

ICPs, including POT, have been added to various other coating materials in order to improve their protection capabilities. The three poly-toluidines have been added to waterborne polyurethane made into a coating on steel [118]. The composite with PMT performed best, with POT significantly lower protection was noticed. A nanocomposite of POT, castor oil, and polyurethane has been proposed as efficient protection showing about 99% inhibition efficiency even after extended periods of time [119, 120]. Reasons for the use of *o*-toluidine or any particular advantage of its use are not mentioned. A further possible advantage of using composites (the term hybrid should be reserved for materials where specific interactions between the constituents add further improvements beyond simple additivity) is improvement of mechanical properties of a polymeric substance by adding mechanically more stable inorganic, mineral components. Such addition may further help to reduce the price of the final protection product. A composite coating

of fly ash and poly(aniline-co-*o*-toluidine) with an epoxy binder has been studied; the advantage of using a copolymer and *o*-toluidine in particular are not mentioned [121]. Such copolymer coating with TiO_2 instead of flash has been examined [122]. A similar composite of such copolymer with chitosan and SiO_2 has been examined; the same question regarding *o*-toluidine remains [123]. 99.52% protection efficiency was noted, still inferior to a coating using 2,3-xylydine instead of *o*-toluidine. ICP nanoparticles of POT, poly-anisidine, and their copolymer added to water-based paints show high corrosion protection efficiencies [124]. Presence of *o*-toluidine did not show any significant advantage.

A composite of CdO and POT coated on mild steel by electropolymerization provided corrosion current reduction by a factor of 1/70 [125]. The use of two constituents both strongly limited by environmental and health limitation yielding a coating of performance below the already established achievements appears to be rather unattractive. POT coated on mild steel by electropolymerization in the presence of ZrO_2 nanoparticles yielded a protection efficiency of 97% [126]. Except for stating, such coating has not been studied before no reason for using *o*-toluidine was provided.

Corrosion protection coatings of zinc and SiC electrodeposited first and subsequently coated with polyanilines have been suggested [127]. A topcoat of POT performed better than poly-*m*-toluidine, but poly-*o*-ethylaniline protected even significantly better. This finding has been confirmed in a similar study by these authors [128].

A composite of POT, nano- ZrO_2 , and epoxy has been tested on steel [129, 130]; the use of *o*-toluidine instead of plain aniline has been justified by the changes of molecular properties afforded by alkyl-substitution at the aromatic ring. No efficiency data were provided; in particular, no support of the claimed beneficial effect of alkyl-substitution was offered. In a similar approach, performance of a composite of epoxy and ZnO could be increased by adding POT up to 98% inhibition efficiency [131]. The enhanced solubility of POT as compared to that of PANI suggested its use. A nanocomposite of alumina-silica-POT added to epoxy as protective coating on carbon steel has been characterized, and at best, 97.5% protection was achieved [132]. With TiO_2 used instead, a protection efficiency of 97.85% was found; increased tortuosity caused by the inclusion of the nanoparticles was suggested [133]. The superior corrosion protection of conducting polyborozirconia(*o*-toluidine) nanostructures added to epoxy coatings on carbon steel has not been supported by experimental evidence [134].

Chemically prepared POT with added SiC nanoparticles has been studied as addition to epoxy as protective coating on iron of unspecified composition [135]. Studies with aqueous 3.5% NaCl corrosive environment indicated a benefit of the SiC addition in terms of increased tortuosity for reactant

diffusion. Protection efficiencies were not provided, from presented data values up to 99% can be estimated.

POT combined with ZnO in waterborne polyurethane provided 96.32% protection efficiency for carbon steel exposed to aqueous 3.5% NaCl solution; the electronic effects of an alkyl-substituent at the benzene ring causing various advantages of the ICP was suggested as reasons for using *o*-toluidine [136]. Superior protection by a composite of POT and MWCNTs has been claimed without providing protection efficiency data [137]. How the enhanced electrocatalytic activity for dioxygen reduction in comparison to simple POT afforded by MWCNTs contributed to this performance remains mysterious. A composite of POT and graphene provided inhibition efficiency for carbon steel up to 99.96% [138]. Various advantageous changes of *o*-toluidine when compared with aniline were invoked as possible reasons of this finding.

Nanocomposite coatings of ICPs with various other constituents for corrosion protection are mentioned in a review on such functional materials [139].

In a somewhat unconventional approach, polymers of the three isomeric toluidines were added at various concentration to aqueous 1 M HCl with mild steel as the corroding material [140]. POT performed poorest. In a very similar approach, a copolymer of aniline and *o*-toluidine with *p*-toluene sulfonic acid anions as counter anions was examined; at 200 ppm, concentration an inhibition efficiency of 96.6% was observed [141]. Reasons for selection of *o*-toluidine were not provided, because albeit small solubility of the copolymer was required; the solubility-enhancing property of *o*-toluidine may have been relevant. A copolymer of aniline and *o*-toluidine was found to be soluble in several organic solvents including dimethylformamide [142]. Small amounts of this solution were added as inhibitor to an aqueous 3 M NaCl solution with carbon steel as sample material; an optimum inhibition efficiency of 70% was obtained. Solubility of the copolymer was the reason for using *o*-toluidine.

Application in sensors and other functional applications

Possible uses of ICP-coating in both chemical and electrochemical sensors have been suggested rather early [5]. The actual function of the ICP depended both on the type of sensor and its operating principle. Further applications as coating beyond corrosion protection not necessarily in a sensor device have been suggested; representative examples will be presented in this section. Initial studies were focused on the most frequently investigated ICPs PANI, polypyrrole, and polythiophene. Given the change of properties, both of the monomer and of the polymer already addressed in previous sections researchers turned their attention to substituted monomers including *o*-toluidine. Sometimes, this

was based on rational considerations, and sometimes, it was just trying, but sometimes, it appears that researchers just repeated previous work started with another monomer now with *o*-toluidine. Given the major flaw of this monomer, particular attention will be focused below as in the preceding sections on the actual benefit of using *o*-toluidine.

Various modes of operation of sensor or sensor-like devices incorporating ICPs and POT in particular have been developed and reported. The increase of electronic conductivity of POT upon exposure to a growing concentration of nitrogen dioxide has been used in a sensor [143]. POT was selected because of its relatively good processability. The actual mechanism of the conductivity change was not elucidated; the change could be reversed by exposure of the sensing element to UV radiation. Electrospun fibers of a composite of polystyrene and camphor sulfonic acid-doped POT have been suggested as sensitive elements for vapors of e.g. water, ethanol, and hexane [144]. Reasons for the use of *o*-toluidine were not given; presumably, solubility of POT required for the electrospinning process was the main argument. PANI and several alkyl-substituted polyanilines including poly(2,3-dimethylaniline) showed changes of electronic conductivity as a function of humidity; the effect was largest with the latter ICP [145]. A cation exchange nanocomposite of POT and It(IV)phosphate has been examined for humidity sensing [146]. Changes in electronic conductance of various ICPs including POT caused by exposure to vapors of various aliphatic alcohols have been attributed to changes of crystallinity [147]. Sensitivity of POT was medium to low by comparison. A composite of poly(*o*-phenylenediamine-*co*-*o*-toluidine)/nitrogen-doped graphene nanoribbons/ionic liquid has been examined for its sensitivity to 4-nonyl-phenol as potential sensor material [148]. Reasons for the use of POT and the selected copolymer were not provided. A composite of POT (with sodium dodecyl sulfate as counter anion) with embedded copper oxide has been as sensor material for amoxicillin [149]. The absence of a previous investigation of this composite for this application seems to be the only reason for using POT. The term selectivity does not even show up.

An optical pH-sensor employing a POT layer as sensitive element showed irreversible behavior suitable only for a single measurement [150].

A composite of POT and MWCNT (which according to the report may have been functionalized in ways difficult to extract and understand from the report) has been proposed as a sensor material for Ce³⁺-ions [151]. Presumably, some sort of amperometric operation was suggested although experiments were performed with a two-electrode electrometer with only one unspecified counter/reference electrode. Significant selectivity of this material was claimed based on a display of the positive-going part of an electrode potential scan obtained with

unspecified experimental parameters. At the same concentration as some other cations, Ce^{3+} -ions provided a slightly larger current than the other cations. How this suggests the claimed selectivity escapes the present authors. Reasons for the use of POT were apparently not even considered, which inhibitors present in *o*-toluidine could be removed by distillation remains a mystery. In a further study, strikingly similar in all aspects to the preceding one suggests a POT/graphene oxide CNT composite as a material selective for Pb^{2+} -ions [152]. The same critical reasoning already outlined regarding the preceding study (except for the irritating details related to distillation of the monomer) applies again.

The ion selectivity of a material, e.g., a membrane, can be utilized in a detector or sensor. A composite of POT and Sn(IV)tungstate turned out to be highly selective for Cd^{2+} -ions [153]. Neither reasons for the use of *o*-toluidine nor for the observed selectivity were offered. The same authors reported high selectivity for Pb^{2+} -ions after addition of MWCNTs to the composite [154]. Reasons for this most significant difference were not even discussed, selection of *o*-toluidine was not addressed. A Hg(II)-selective electrode using POT-zirconium phosphoborate has been reported [155]. A composite of POT and Th(IV)phosphate offered some selectivity for Hg^{2+} -ions; it could be used in a PVC-membrane ion-selective electrode [156].

Selectivity towards Pb^{2+} -ions useful for an ion-selective electrode was found for a nanocomposite of poly(pyrrole-co-*o*-toluidine)/ CoFe_2O_4 [157]. In a very similar work, this copolymer was combined with cross-linked single-wall carbon nanotubes and nanoparticles of NiFe_2O_4 yielded a material showing sensitivity towards Fe^{3+} -ions in an amperometric sensor setup [158]. Beyond the very extraordinary sensor performance claimed in the report, selectivity is apparently murky at best. In a further variation of this work, the copolymer was combined with CoFe_2O_4 and chitosan yielding the suggestion of a Co^{2+} -ion-sensitive material [159]. Given the striking similarity to the two previous reports by the same author, it is not surprising that the claimed suitability for sensor purpose is dubious at best. In a report otherwise difficult to understand a nanocomposite of POT with Ce(III) tungstate and CNTs, some selectivity to Pb^{2+} -ions was noticed [160]. *o*-Toluidine was apparently selected by some sort of coincidence. A composite of gold nanoparticles, graphene oxide, and poly(aniline-co-*o*-toluidine) showed sensitivity towards Cr(VI)-ions in an amperometric setup [161]. Reasons for selection of this ICP are not even considered. A composite of POT and zirconium(IV)iodosulfosalicylate shows ion-selectivity for Cr^{3+} -ions and has been suggested for use in a membrane electrode [162]. No particular reason for using POT has been indicated.

A non-enzymatic glucose sensor based on POT nanofibers modified with gold and copper nanoparticles has been

described [163]. Apparently, better processability of POT as compared to PANI suggested the use of this ICP.

Although the title suggests that only POT was the sensitive material in a glucose sensor actually glucose oxidase entrapped in the ICP was the main agent in an amperometric sensor showing poor stability [164]. An amperometric glucose sensor based on glucose oxidase entrapped in films of POT, poly(*o*-anisidine), and their copolymer has been tested [165]. A slightly faster response was found with POT. With aniline instead of *o*-anisidine in an analogous study, the fastest response was found with PANI [166]. Finally, these authors considered a terpolymer of said three comonomers [167]. Because results were somewhat surprisingly not compared to those obtained with the homo- and copolymers used in the previous studies any reasons for using *o*-toluidine remain unknown. Neither reasons for the observed selectivity nor for the use of *o*-toluidine were offered. A nanocomposite of POT and carbon nanotubes has been proposed as a biosensor platform and has been tested as an amperometric urea sensor after immobilization of urease in the ICP [168]. Compared with other ICPs studied also POT provided the strongest signal.

A modifying layer of POT applied to a carbon paste electrode showed significant catalytic activity for nitrite reduction possibly useful in a sensor application [169]. Reasons for this particular activity were not identified.

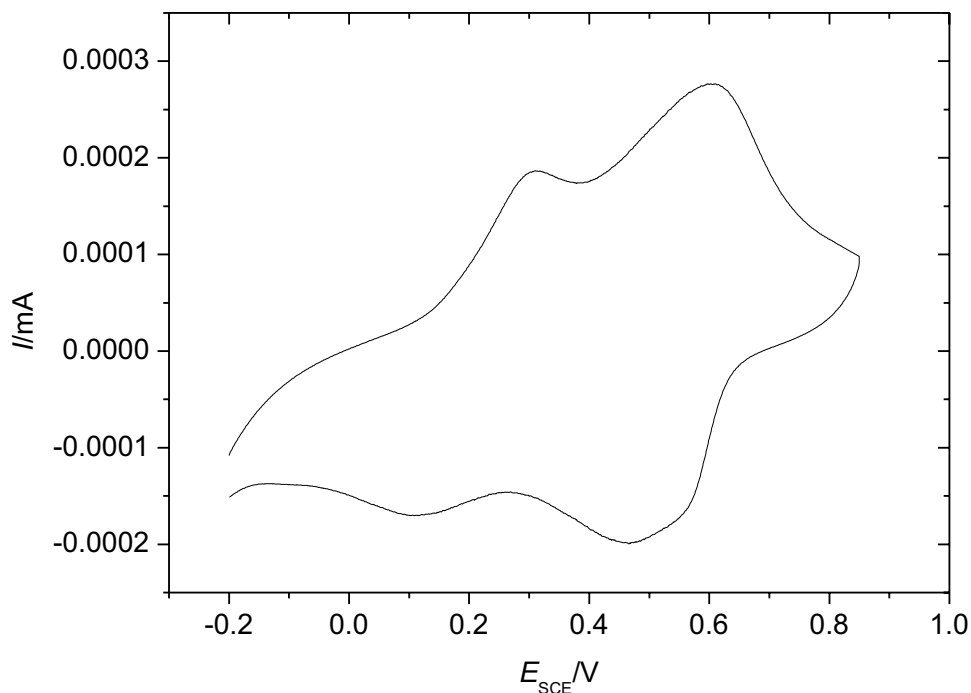
A review of composite materials including POT for use in sensors is available [170]. A comparison of the behavior of ICPs prepared from some simple aromatic amines as permselective membranes has been reported, no particular advantages of POT were noticed [171]. Without suggesting a particular reason for selecting just POT, it has been suggested as a permselective membrane for hydrogen-peroxide-based biosensors [172].

Application in supercapacitors and secondary batteries

ICPs have been suggested as active masses in electrodes of batteries (both primary and secondary ones) almost immediately after the discovery of their electrochemical redox activity [173]. A typical CV of a gold electrode coated with chemically synthesized POT [72] is shown in Fig. 6; the suggested structural transformations during the first redox process (at lower electrode potentials) are shown in Fig. 7.

Following the advent of supercapacitor research and development, these materials were also examined for this application [174]. Beyond the parent molecules (aniline, pyrrole etc.), their substituted relatives have been polymerized both chemically and electrochemically and examined as active masses. Substitution of the monomers with different groups may affect the oxidation potentials of the monomers relevant in particular when electropolymerizing the material.

Fig. 6 CVs of a POT-coated gold sheet electrode in an aqueous solution of 0.5 M H₂SO₄ at $dE/dt = 0.05 \text{ V s}^{-1}$



As has been reported elsewhere taking substituted thiophene as an example, the redox behavior of the ICP can also be affected [175–180]. Methods from theoretical chemistry have been employed to understand observed effects; they may help to predict properties of compounds not yet studied. Because the electrode potential of redox transitions in the ICP will directly affect the cell voltage of a supercapacitor, such options are practically relevant.

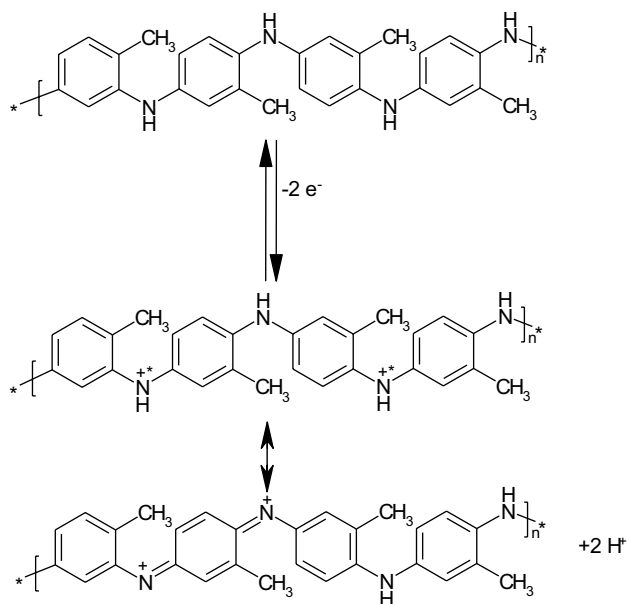


Fig. 7 Simplified reaction scheme of the first redox transition of POT

Preparation of copolymers is a further venue for fine-tuning properties of an ICP as reviewed elsewhere [2]. Among the examined monomers, aniline and its substituted relatives are particularly prominent. *o*-Toluidine has been polymerized chemically [181] and used as positive electrode material in a secondary battery with a negative zinc electrode and a neutral electrolyte solution of ZnCl₂ [182]. Other aniline-related monomers provided only electronically insulating polymers deemed not suitable for this application. The performance of the material was considered to be promising, but so far, no further development of this application has been observed. Certainly, the observed sufficiently high electronic conductivity of the polymer (see also [93]) is helpful because, otherwise, conducting additives like acetylene black must be added. Nevertheless – in the absence of any reason why just the *o*-substituted compound enables this conductivity – similar molecules should be examined for both conductivity and electrochemical redox activity.

Carbon fabric has been coated with POT by electropolymerization; the performance of the obtained electrode in a supercapacitor has been examined [183]. For comparison coating with polyaniline, PANI was examined. The improved performance of POT was attributed to its higher electronic conductivity enabling utilization of thicker polymer layers at higher currents. Because no attempt has been made to substantiate this claim, the discrepancy with respect to an earlier comparative study [93] of the behavior of polymers obtained electrochemically from various alkyl-substituted anilines unfortunately overlooked later remains. According to the earlier findings, PANI grows faster than POT; this has

been attributed to the influence of the methyl-substituent on the electrooxidation kinetics. Given the inherent problem of absolute conductivity measurements with ICPs, the authors in [93] did not attempt to claim such values; the later authors in [183] ignored this aspect completely. Finally, they observe experimentally evidence suggesting a lower internal resistance of their supercapacitor cell. In the following discussion, they attribute this to a more open structure of POT when compared to that of PANI, i.e., not to the inherent conductivity of the ICP at all. Such morphology can possibly also be obtained by changing the electropolymerization protocol from e.g., potentiodynamic to potentiostatic or a potential step method [184] or to a galvanostatic protocol [185] or by using another anion present during electropolymerization [186–188]. POT obtained by chemical polymerization has been suggested as active supercapacitor electrode material because its solubility seems to enable coating of a substrate with POT making the use of a binder unnecessary [189]. The recorded performance was attributed to the use of dodecylbenzene sulfonic acid as a counter anion showing particularly efficient interaction with POT. This anion is also employed in preparing soluble PANI [84, 85]; thus, there may be no need to use POT to obtain the stated advantages. A copolymer poly(aniline-co-*o*-toluidine) has been examined as supercapacitor electrode material [190]. Reasons for the use of *o*-toluidine and the studied copolymer were not provided.

Composites of an ICP with a conducting material may help to overcome or at least ameliorate the problems caused by the electrode-potential dependent electronic conductivity of an ICP. Preparation of a nanocomposite of chemically synthesized poly(*o*-toluidine) and multiwalled carbon nanotubes MWCNTs utilized the improved processability, i.e., solubility, of POT as compared to PANI [191]. A symmetric supercapacitor with two electrodes of this nanocomposite and an aqueous electrolyte solution of 1 M sulfuric acid showed 12.4% capacitance loss after 2000 cycles. A composite of chitosan and POT was prepared by chemical polymerization of the latter in an aqueous solution containing a small concentration of chitosan. The presence of both constituents in the composite was verified by infrared spectroscopy; the actual fractions were not determined. The behavior as supercapacitor electrode was examined, but a “current sensing capability” was considered the most prominent feature. Reasons for selection of *o*-toluidine as the starting monomer were not provided. Because the particular sensing capability quite obviously is related to shrinking and swelling of an ICP during its redox transformation, a particular need for this monomer is not obvious.

Miscellaneous observations and applications

ICPs have attracted attention as electrocatalysts for various electrode reactions possibly of interest in electrochemical

energy conversion [173] or in electrosynthesis. Instead of plain PANI, polymers of substituted anilines have been considered candidate materials assuming that changes in the molecular and electronic structure caused by the substitution may also affect electrocatalytic behavior. In addition, substitution may affect stability. For unknown reasons, POT electrodeposited on a platinum support showed considerable electrocatalytic activity in benzyl alcohol oxidation [192].

POT has been used as support for electrocatalysts employed e.g., in fuel cell electrodes. Like with other ICPs, its conceivable function as an electronically conducting binder was the main purpose, in addition to increased stability because e.g., impeded agglomeration of catalysts particles or their loss into the electrolyte solution may be of interest. Platinum microparticles deposited onto POT following different electrochemical protocols have been tested as catalysts for the electrooxidation of formic acid [193, 194]. Although no specific current densities with respect to the electrochemically active platinum surface [195], the composite electrodes provided rather expectedly larger currents than a smooth platinum wire; POT itself did not show any electrocatalytic activity. Reason for using *o*-toluidine and a comparison with a similar material based on PANI was not offered. In a comparative study of ICPs chemically polymerized from a few substituted anilines, their effect on incorporated platinum particles has been examined [196]. An increase of currents due to isopropanol oxidation was assigned to enhancing electronic interaction between metal and ICP; the effect was highest with POT. Cu²⁺-ions incorporated into POT showed electrocatalytic activity towards oxidation of 3-ethoxy-4-hydroxy-mandelic acid into ethylvanillin [197]. Reasons for the choice of POT and of the substrate are not evident.

Nickel ions dispersed in POT prepared in the presence of Triton X-100 surfactant on MWCNTs act as a low-cost catalyst for electrooxidation of methanol [198]. The absence of reports on the use of POT for the studied application is the only reason provided for the use of *o*-toluidine. In a variation of this study, using formaldehyde instead of methanol leaves the same conclusion [199]. Ni(II)-ions incorporated into POT layers electropolymerized on a glassy carbon electrode modified with polyvinyl alcohol showed significant electrocatalytic activity towards the oxidation of formaldehyde in alkaline electrolyte solution [200]. A reaction mechanism involving the Ni(II/III)-redox couple acting as a mediator has been proposed whereas the particular reason to use *o*-toluidine has not been discussed.

Cobalt deposited on ordered mesoporous carbon embedded in POT provides high electrocatalytic activity for dioxygen reduction with low sensitivity towards methanol possibly migrating towards the cathode of a direct methanol fuel cell [201]. Reasons for the selection of POT were not provided.

Reasons for the observed mercury ion selectivity of a composite of POT and Zr(IV)tungstate, in particular of *o*-toluidine, have not been reported [202]; the same reasoning applies to a mercury ion-sensitive composite of poly(*o*-toluidine)@Sn(II)silicate/CNT² [203]. A nanocomposite of POT and Zr(IV)phosphate has been studied and suggested for a pesticide-(2,4,5-trichlorophenoxy acetic acid)-sensitive membrane electrode; reasons for the selection just of POT were not even considered [204].

The electrochromic behavior of a composite of WO₃ and a copolymer of aniline and *o*-toluidine has been reported; the reasons for using a copolymer instead of homopolymers (see [205]) are not apparent [206]. The electrochromic performance of oligoaniline-containing polyurea's end-capped with various functional groups has been examined; the use of *o*-toluidine as an end-group apparently has no particular advantage [207]. ICPs of *o*-, *m*-, and *p*-toluidine have been tested for their electrochromic response [208]. Expectedly, *p*-toluidine yielded only a poorly behaving material, *o*-, and *m*-toluidine yielded basically equivalent ICPs. Spectral changes of three ICPs made from aniline, *o*-methoxyaniline, and *o*-toluidine caused by ammonia formed by several animal products have been explored for application in a product freshness sensor [209]. PANI performed better than POT.

For the reasons outlined above, copolymers of *o*-toluidine with various comonomers have been suggested and examined. Results are sometimes difficult to appreciate when e.g., authors use aniline, *o*-toluidine, and *o*-anisidine as synonyms [210].

Conclusions

Reasons for the selection of *o*-toluidine as an inhibitor, a monomer, or a comonomer are frequently not provided; only speculation (without scientific merit in the present context) might shed light on the researchers' reasoning. There are nevertheless some arguments repeatedly addressed suggesting consideration of *o*-toluidine. Electronic effects depending on the substitution pattern (*o*- vs. *m*- and *p*-) have been invoked in particular in corrosion studies. Because inhibition efficiencies differ strongly for studied metals and depend on the composition of the corrosive environment no general conclusion is possible, but in most cases, *o*-toluidine is not the most efficient one anyway. Thus, there seems to be no need to use this inhibitor at least in these cases. With ICPs, the use of *o*-toluidine either as single monomer or comonomer the increased solubility and thus simplified processability of the polymer have frequently been invoked as a major

advantage. Different polymerization protocols also yielding soluble ICPs may provide an alternative without *o*-toluidine. In case of protection efficiencies significantly below results reported elsewhere, an attempt to speculate about reasons for using *o*-toluidine was deemed not necessary.

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² In the report, the name poly(*o*-methoxyaniline) is used although this is certainly not a synonym of *o*-toluidine.

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