



# *In situ* confocal Raman micro-spectroscopy and electrochemical studies of mussel adhesive protein and ceria composite film on carbon steel in salt solutions



Fan Zhang<sup>a</sup>, Tore Brinck<sup>b</sup>, Birgit D. Brandner<sup>c</sup>, Per M. Claesson<sup>a,c</sup>,  
Andra Dedinaite<sup>a,c</sup>, Jinshan Pan<sup>a,\*</sup>

<sup>a</sup> KTH Royal Institute of Technology, School of Chemical Science and Engineering, Department of Chemistry, Division of Surface and Corrosion Science, Drottning Kristinas väg 51, SE-100 44, Sweden

<sup>b</sup> KTH Royal Institute of Technology, School of Chemical Science and Engineering, Department of Chemistry, Division of Applied Physical Chemistry, Teknikringen 36, SE-100 44, Sweden

<sup>c</sup> SP Technical Research Institute of Sweden, Chemistry, Materials and Surfaces, P.O. Box 5607, SE-114 86 Stockholm, Sweden

## ARTICLE INFO

### Article history:

Received 30 April 2013

Received in revised form 8 May 2013

Accepted 8 May 2013

Available online xxx

### Keywords:

*Mefp-1*

Ceria nanoparticle

Corrosion inhibition

*In situ* confocal Raman micro-spectroscopy

Electrochemical impedance spectroscopy

## ABSTRACT

Thin films composed of *Mefp-1* and ceria nanoparticles have shown an increasing corrosion inhibition effect with time for carbon steel in acidic aqueous solutions containing phosphate, which motivates a detailed study of the inhibition mechanism by *in situ* confocal Raman micro-spectroscopy (CRM) and electrochemical impedance spectroscopy (EIS) measurements. The presence of both CeO<sub>2</sub> and ferric oxides in the thin composite film was demonstrated by X-ray photoelectron spectroscopy analysis. The Raman spectra assisted by DFT calculations suggest that *Mefp-1* forms tri-Fe<sup>3+</sup>/*Mefp-1* complexes and binds to ceria nanoparticles in the composite film. The *in situ* CRM measurement allow us to follow the development of corrosion products. The measurements show a mixture of Fe oxides/oxyhydroxides, and also indicate that ferrous oxides may be further oxidized by the composite film. Moreover, phosphate ions react with the Fe ions released from the surface to form iron–phosphate deposits, which become incorporated into the corrosion product layer and the composite film. The EIS measurements suggest a layered surface structure formed by the initial *Mefp-1*/ceria composite layer and the corrosion products/iron–phosphate deposits. These measurements also demonstrate the greatly increased inhibition effect of the composite film in the presence of the phosphate ions. The consistent CRM and EIS results suggest that the iron–phosphate deposits heal defects in the composite film and corrosion product layer, which results in a significantly improved corrosion inhibition of the *Mefp-1*/ceria composite film during initial and long term exposure.

© 2013 Elsevier Ltd. All rights reserved.

## 1. Introduction

Due to legislation and increased awareness of ecological and environmental issues, a range of the traditional anti-corrosion approaches become obsolete. Thus, development of new type of corrosion inhibitors, preferably with ‘universal’, ‘green’ and ‘smart’ properties, are urgently needed for practical applications. A mussel adhesive protein (MAP) derived from marine mussel *Mytilus edulis* has attracted considerable attention in recent years for its universal adhesive, film-forming, and corrosion inhibiting properties [1–9]. It has been shown di-hydroxyphenylalanine (DOPA) is the primary residue of the MAPs responsible for both adhesion and cohesion, via chemical interactions including hydrogen bonding [3,10], covalent

bonding [11], metal-liganding [12–15], and cross-linking [16,17]. *Mefp-1* is the first polyphenolic protein to be characterized from the *M. edulis* foot [1,18], and it is also the only protein associated with the protective outer cuticle of byssal threads including the plaques [19]. *Mefp-1* consists of a large number (75–80) of repetitive decapeptide units and contains a high level 10–15 mol% of DOPA [20].

Cerium salts have been investigated as environmentally friendly corrosion inhibitors and have shown a certain inhibition effect [21]. For instance, by adding a ceria (CeO<sub>2</sub>) thin film and a fluoride coating on magnesium alloys, the corrosion resistance was improved by two orders of magnitude compared to the uncoated substrate [22]. The impact of nanoparticles on human health is an issue of concern. In this regard, it was reported that ceria nanoparticles are not cytotoxic but instead protect cells from oxidation insult [23]. In our previous study [24], a thin composite film of *Mefp-1* and ceria nanoparticles was shown to exhibit significant corrosion

\* Corresponding author. Tel.: +46 08 790 6739.

E-mail address: [jinshanp@kth.se](mailto:jinshanp@kth.se) (J. Pan).

protection for carbon steel in NaCl containing phosphoric acid. A combination of both *ex situ* and *in situ* techniques has been used to investigate the film formation, structure and corrosion inhibition performance. Remarkably, the corrosion inhibition efficiency was found to increase dramatically with exposure time. However, the reason for the increasing inhibition effect has up to now not been clarified.

Iron-based metals are widely used, and their corrosion behavior in a variety of environments has been investigated. It is well known that the corrosion products of iron in aqueous environment are mostly  $\text{Fe}_3\text{O}_4$ ,  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\alpha\text{-FeOOH}$ , and  $\gamma\text{-FeOOH}$  [25–29]. The nature of the oxides formed and developed during a corrosion process is of great importance for the corrosion behavior. On the other hand, inorganic phosphate species are generally considered as environmental friendly and effective corrosion inhibitors for iron and carbon steels in near neutral solutions [30–32]. Phosphate species strongly interact with dissolved iron ions and form iron–phosphate compounds with low solubility that precipitate at the surface [30,33,34]. This iron–phosphate layer on its own does not provide efficient corrosion protection due to the porous structure. However, phosphate species are widely used in combination with paints to enhance the corrosion resistance of iron base metals [35]. It is thus plausible that phosphate species may also act synergistically with the *Mefp-1* corrosion inhibitor. Therefore, clarifying the mechanisms of the inhibiting effect of phosphate species, especially their synergistic action with pre-formed composite film of *Mefp-1* and ceria nanoparticles, has important theoretical and practical significance.

Electrochemical impedance spectroscopy (EIS) has been widely used to characterize interfacial electrical properties of steels in aqueous environments [36]. EIS is a non-destructive and sensitive technique, and the phase angle plot of the impedance spectra may provide information of the interfacial structure [37,38]. Confocal Raman Micro-spectroscopy (CRM) is a powerful *in situ* analysis method that enables quick and unambiguous identification of compounds present in surface layers [39]. Moreover, by using density functional theory (DFT) calculations the spectroscopic analyses can be developed further for extracting additional chemical details of the composite film. X-ray photoelectron spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is a highly surface sensitive and powerful tool for chemical surface analysis, allowing quantitative analysis of elemental composition and chemical states [40]. In this study, we applied all these techniques to obtain comprehensive information on the corrosion inhibition mechanisms of the *Mefp-1*/ceria composite film, and to clarify the effect of the phosphate species added in the solution. Such information is required for further improvement of the composite film, and for development of new environmental friendly corrosion inhibitors based on *Mefp-1* and ceria nanoparticles.

## 2. Materials and methods

### 2.1. Protein and solutions

The mussel adhesive protein, *Mefp-1*, with a purity of 92 wt.% (the impurity is mainly aggregation/degradation products of *Mefp-1*) was supplied by Biopolymer Products AB (Gothenburg, Sweden), in the form of a 25 mg/ml aqueous solution containing 1 wt.% citric acid. It was stored in darkness at +4 °C.

The ceria nanoparticles (NANOBYK-3810) were supplied by BYK Additives and Instruments (Wesel, Germany). The diameter of the ceria particles is 10 nm with a narrow size distribution according to the supplier, and this was confirmed by dynamic light scattering measurements. The nanoparticles were delivered as dispersion in

water and stored at room temperature. The solution was sonicated for 10 min before the experiment to ensure good dispersion.

The aqueous solutions used for the corrosion tests contained 0.1 M NaCl with or without 0.2 M  $\text{Na}_2\text{HPO}_4$ . A small amount of 10% HCl solution was added into the  $\text{Na}_2\text{HPO}_4$  containing solutions to adjust pH to that of the NaCl solution (ca. 6–6.5).

All chemicals used for preparing solutions were of analytical grade and the water was of Milli-Q quality.

### 2.2. Carbon steel substrates

The carbon steel substrates were cold rolled low carbon steel (DC 01, 1.0330, supplied by IVF, Sweden). The nominal composition of the steel is Fe, 0.12 wt.% C, 0.60 wt.% Mn, 0.045 wt.% P, 0.045 wt.% S. The steel sheet samples were wet ground with SiC grinding paper successively up to 1200 grids, and then cleaned ultrasonically with ethanol.

### 2.3. Deposition of *Mefp-1*/ceria nanoparticle composite films

The *Mefp-1*/ceria composite films were prepared by sequential adsorption. The first layer was obtained by *Mefp-1* adsorption using an aqueous solution containing 100 ppm *Mefp-1*, 1 wt.% citric acid and 50 mM NaCl at pH 8–9. The next layer was formed by adsorption from an aqueous solution containing 500 ppm ceria nanoparticles. Subsequent adsorption steps were carried out from solutions with the same composition, alternating between the *Mefp-1* and the ceria nanoparticle containing solutions. The substrate was immersed for 40 min in each solution to ensure sufficient adsorption. This procedure was repeated 4 times for each solution type to form a composite film on the sample surface. The immersion procedures were carried out at room temperature and the solutions were renewed between each step. After completing the deposition process, the sample was gently rinsed in pure water, and then kept in air at room temperature overnight before being used for further studies.

### 2.4. XPS analysis

XPS was employed to identify ceria and iron oxide components in the *Mefp-1*/ceria composite film. Spectra were recorded using a Kratos AXIS Ultra<sup>DLD</sup> X-ray photoelectron spectrometer (Kratos Analytical, Manchester, UK) with a Mg X-ray source. In the analysis low-resolution broad binding energy spectra were recorded to detect all elements present in the surface layer. The relative surface composition was obtained from quantification of high-resolution spectrum over a narrow binding energy interval for each element. The analysis area was about 1 mm<sup>2</sup> (most of the signal arising from an area of 700  $\mu\text{m} \times 300 \mu\text{m}$ ). The analysis depth depends on the analyzed material, and is about 10 nm for polymers and lower for metal and metal oxides (ca. 5 nm).

### 2.5. *In situ* CRM analysis

The *in situ* CRM measurement were performed on carbon steel surfaces coated with the *Mefp-1*/ceria composite film in 0.1 M NaCl solutions with or without addition of 0.2 M  $\text{NaH}_2\text{PO}_4$ , respectively. Measurements on uncoated carbon steel surfaces were also performed for comparison. In order to identify changes in the surface layer with time, *in situ* CRM measurements were performed on the samples with and without the composite film, respectively, after different times of exposure.

The CRM instrument was a WITec alpha 300 system (WITec GmbH, Germany), equipped with a 532 nm laser for excitation, and an oil immersion objective with 100 $\times$  magnification and numerical

Download English Version:

<https://daneshyari.com/en/article/6616775>

Download Persian Version:

<https://daneshyari.com/article/6616775>

[Daneshyari.com](https://daneshyari.com)