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Effect of hydrogen carbonate and chloride on zinc corrosion investigated by a scanning flow cell system

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ABSTRACT

A scanning flow cell with time-resolved downstream detection system is employed to analyse the corrosion behaviour of zinc in weakly alkaline hydrogen carbonate-containing electrolytes. Since zinc is usually exposed to varying environmental conditions, dynamic electrolyte exchange is used to investigate the impact of changing electrolyte constituents over time for the first time. The polarization resistance was monitored with galvanostatic pulses. Anodic current steps are applied to correlate the overall net current to the rate of precipitate formation. The results are complemented by investigations of the morphological features of the corroded surfaces and precipitates utilizing broad ion beam cross-sectioning techniques.

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1. Introduction

Zinc based coatings are of tremendous industrial importance and have been used for sacrificial protection of steel for decades. Since corrosion under environmental conditions is a highly complex and diverse process, many techniques have been utilized to study, simulate and predict the effect of single parameters on the performance of zinc based protective coatings [1–4]. Under wet conditions, the electrolyte composition represents the most important parameter that determines the corrosion behaviour [3,5]. In particular the (local) pH is decisive for the formation and stability of precipitates that may passivate the surface [5–7]. Owing to the amphotheric character of zinc hydroxides (and oxides), these precipitates are stable only in a limited pH range around 9–10 [3,8,9]. Furthermore, the ubiquitous chloride and carbonate have an immediate impact on the electrochemical behaviour [10] and the solid reaction products formed [11]. In presence of CO_2 and/or carbonates a variety of insoluble corrosion products was reported [3,10,12,13]. An increased stability range of carbonate-containing zinc precipitates along the pH axis is indicated by the combined Pourbaix diagram [10]. It has been calculated that a total concentration of “carbonates” ($H_2CO_3 + HCO_3^{-} + CO_3^{2-}$) larger than $10^{-2.4}$ M [8] leads to an extension of the passivity domain of zinc towards neutrality in comparison to zinc passivation by formation of zinc hydroxide films [8,12–15]. This observation was attributed to the precipitation of solid $ZnCO_3$ in absence of any aggressive ions. Even though well studied individually, only few studies address the effect of the combined electrolyte system containing both chloride and carbonate in different concentrations [11,16–19]. In this regard, it was reported that already low chloride contents prevent passivation. Furthermore it was observed that high amounts of carbonate in comparison to chloride result in a less pronounced localized corrosion [11,12,16,20]. This was attributed to coverage of anodic sites and thus hindering of anodic dissolution [12]. In particular, the protective character of zinc hydroxy carbonate precipitates is controversial [11,16,19,21–24], however, this may also depend on the experimental conditions. Thus, the presence of specific corrosion products and their influence on reactivity and change in corrosion behaviour was subject of recent publications [17–19,25]. Accordingly, the effect of carbonate ions in near-neutral pH is critical for zinc corrosion in general. In this respect, the stability of the formed corrosion products and their impact on both anodic and cathodic reaction kinetics is of immediate interest.

The objective of this study is to investigate rapid changes in the corrosion behaviour, e.g. initial attack on the native oxide layers,

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buildup of precipitates and transformations of the surface layers after electrolyte changes, rather than to monitor long term corrosion behaviour. Furthermore, we want to gain fundamental insights into the corrosion (protection) mechanism of zinc in hydrogen carbonate- and chloride-containing electrolytes. In particular, dynamic electrolyte change is utilized to investigate the corrosion behaviour of carbonate-containing electrolytes on pre-corroded surfaces. Several interrelated parameters like the effect of buffer concentration, the pH value and the role of precipitates are discussed with regard to the corrosion behaviour.

For this purpose we have developed a fully automated experimental setup that provides dynamic electrolyte exchange even during the measurement and thereby allows a comprehensive investigation of the individual effects of different electrolyte constituents. The setup is based on an innovative micro electrochemical scanning flow cell (SFC) system with time-resolved downstream analysis of the corrosion products [26] that is able to deal with the complex interrelation between the variable electrolyte composition and the corrosion behaviour. The SFC setup offers two additional advantages, namely, (1) the flow improves control of the electrolyte composition as no zinc accumulates over time, consumed oxygen is replaced and pH changes are counteracted and (2) the automation and scanning facility allows a quick and easy sample exchange and therefore highly reproducible experiments on fresh surfaces. Both the electrochemical response and the dissolution rate, measured by downstream UV–vis detection of zinc, are recorded simultaneously to provide a comprehensive picture of the underlying processes. The online detection of dissolved species is of significant benefit for many electrochemical investigations, as it enables a distinction between the dissolved and precipitated form of species by distinguishing the overall net current from the dissolution of specific elements, as outlined by several authors [26–32]. Since precipitation of corrosion products directly affects the reactivity at the zinc surface, a galvanostatic pulse method is employed complementary to the online detection to monitor this. The chemical composition of the corrosion products in the precipitate films have been identified by Raman spectroscopy. Finally, broad ion beam cross-sectioning techniques are employed to directly study the morphological structure of the corrosion products and their spatial distribution along the surface of the sample.

2. Experimental

2.1. Experimental setup

The experimental setup (Fig. 1) provides up to 6 different electrolyte reservoirs, each operated by a pinch valve to control electrolyte flow. Liquid level sensors (OLT series, First Sensor AG, Munich) are employed to maintain a constant filling level of the reservoirs and therefore keep a constant hydrostatic pressure. This is particularly crucial to form a stable meniscus when the cell is lifted from the sample since the electrolyte is sucked through the SFC. Therefore, changes of hydrostatic pressure would either lead to leakage of the cell or air influx. The sample positioning is achieved by a xyz-translation stage (3× M-403.6 DG, Physik Instrumente GmbH & Co. KG, Karlsruhe). An in-house developed LabVIEW program controls all components simultaneously, including sample positioning, electrolyte composition and flow, electrochemical data acquisition, and downstream Zn detection [33].

Scanning Flow Cell The present scanning flow cell (SFC, Fig. 1, inset) is based on a previous SFC [26], however, made of Teflon (PTFE) to reduce adsorption of precipitates. The contact area on the substrate (0.224 mm^2) is confined by a silicone sealing (thickness: 80 μm). The flow rate for all experiments is 30 μL min^{-1}. An additional channel is designed for injection of hydrochloric acid (0.1 M HCl, 2 μL min^{-1}) to prevent corrosion products from precipitating in the downstream channel (particularly in neutral to near alkaline electrolytes). Local acidification is found to be a highly efficient way to address this problem. A platinum wire at the inlet of the flow cell is used as counter-electrode, while a Ag/AgCl macro reference electrode (LL ISE Reference, Metrohm AG) is connected to the downstream channel. Zinc was detected downstream by UV–vis detection using zincon as complexing agent as described previously [29,34]. An online electrolyte degasser is introduced before the UV–vis cell to remove bubbles from the flow system.

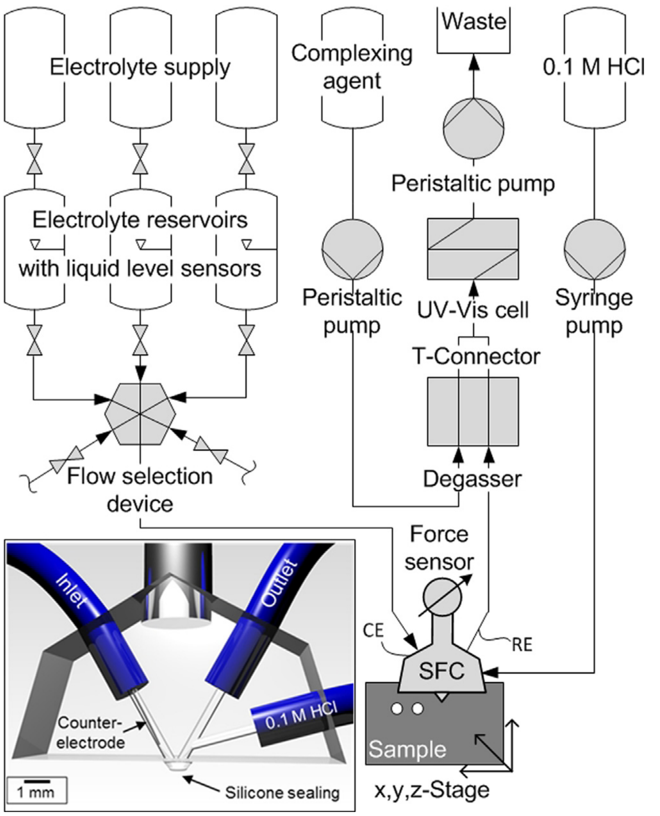

Fig.1. Schematic representation of the experimental setup, inset: the Scanning Flow Cell with injection channel for hydrochloric acid (0.1 M HCl).

2.2. Sample preparation

A 25 mm × 25 mm piece of 2 mm thick zinc foil of 99.95 % purity (Goodfellow GmbH, Bad Nauheim, Germany) is polished with SiC grinding paper to 4000 grit and finally polished with a 1 μm diamond suspension. The surface is repeatedly washed with ultrapure water and ethanol (p.a. grade, Merck KGaA, Darmstadt, Germany) and finally dried in a cold stream of argon.

2.3. Electrolytes

The electrolytes (Table 1) used in this study are prepared from aerated ultrapure water (18.2 MΩ, PureLab Plus, Elga, Celle, Germany), and p.a. grade NaCl and $NaHCO_3$ (Merck). The concentrations of hydrogen carbonate and the resulting pH values of the solutions are listed in Table 1. The (maximum) concentration of soluble Zn species in equilibrium with precipitates is calculated using medusa/hydra [35] for the given pH and composition. In the presence of hydrogen carbonate, the zinc solubility is limited by precipitation of hydrozincite. In absence of hydrogen carbonate

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