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## **ACCEPTED MANUSCRIPT**

# In situ monitoring of the localized corrosion of 304 stainless steel in FeCl<sub>3</sub> solution using a joint electrochemical noise and scanning reference electrode technique

Cheng Wang<sup>a</sup>, Yangzhi Cai<sup>a</sup>, Chenqing Ye<sup>a</sup>, Shigang Dong<sup>b</sup>, Xinshuo Cai<sup>c</sup>, Yanhui Cao<sup>a</sup>, Changjian Lin<sup>a,b\*</sup>

E-mail:cjlin@xmu.edu.cn.

**Abstract:** Electrochemical noise (ECN) has been adopted as a powerful method of studying early-stage corrosion, but there is a lack of direct in situ evidence to prove the correlation between ECN data and visual corrosion behavior. The advanced scanning reference electrode technique (SRET) assisted by electrochemical scanning tunneling microscopy (ECSTM) can detect local active sites of micro corrosion and follow their initiation and development, and can provide experimental evidence of localized corrosion at the same time as the system is monitored by ECN. To further understand the localized corrosion mechanism of metals, an in situ strategy (ECN/SRET) was developed and used to detect rapid initialization of active corrosion sites, and follow the evolution of pitting corrosion. It is expected that the ECN/SRET combination will prove to be a powerful tool for in-depth studies of localized corrosion.

**Keyword:** In-situ; Localized Corrosion; Electrochemical Noise; Scanning Reference Electrode Technique;

#### 1.Introduction

Electrochemical noise (ECN) has been utilized to study localized corrosion behavior since the 1960s due to its high sensitivity to electrochemical fluctuations [1-3]. ECN requires a high level of ability to distinguish time and frequency without the prerequisite of stationarity or linearity [4-6]. A wavelet method is frequently used to analyze ECN data. Different timescales of current and potential signals could be ascribed to diffusion, activation or mixed controlled processes. The timescale with the highest relative energy will usually reflect the dominant corrosion process; the shorter timescales (high frequency) are correlated with relatively fast processes and the longer timescales (low frequency) to relatively slow processes. General corrosion is dominated by long timescale processes, while localized corrosion is dominated by short timescale processes [7-9].

Nevertheless, the wavelet method could not produce the expected direct frequency decomposition of ECN signals at a particular time because the primary function and the number of scales are user-defined, leading to different results, affecting the collection of real corrosion information. The Hilbert-Huang transform (HHT) [10], which has been applied in a wide range of fields, was firstly used by Homborg et al. to analyze ECN signals in corrosion studies [11]. HHT is

<sup>&</sup>lt;sup>a</sup> State Key Laboratory for Physical Chemistry of Solid Surfaces, and College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

<sup>&</sup>lt;sup>b</sup> College of Energy, and School of Energy Research, Xiamen University, Xiamen, 361102, China.

<sup>&</sup>lt;sup>c</sup> Department of Electronic Engineering, School of Information Science & Technology, Xiamen University, Xiamen 361005, China

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