Current oscillations in the anodic dissolution of silicon: On the origin of a sustained oscillation on the macroscopic scale

J.-N. Chazalviel [*,1], F. Ozanam

Physique de la Matière Condensée, Ecole Polytechnique, CNRS, 91128 Palaiseau, France

A B S T R A C T

The damped current oscillations observed in the anodic dissolution of silicon in fluoride electrolyte have been attributed to a sustained current oscillation on the local scale. However, the possibility of a sustained oscillation on the macroscopic scale has been a subject of controversy. Here, through a combined simulation/analytical probabilistic analysis, we examine whether an interaction between the various locations on the electrode surface may lead to a macroscopic oscillation of the total current. We find that a short-range interaction cannot lead to a synchronisation of the oscillation over the surface of a large electrode. Such a synchronisation might however be obtained on small electrodes, or with appropriate values of the system parameters. The examination of existing data in the literature rather points to a macroscopic oscillation induced by global coupling through extrinsic resistances in series with the electrode.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Electrochemical oscillations have always been a source of excitement in the electrochemical community [1,2]. In the last twenty years there has been a special interest in the unusual behaviour encountered in the electrochemical dissolution of silicon in dilute fluoride electrolytes [3–9]. In a potential range 3–10 V vs SCE, the interface tends to exhibiting an oscillatory behaviour, consisting of either current oscillations under potentiostatic control or potential oscillations under galvanostatic control. Numerous works have been devoted to explain this behaviour, and trace it back to a microscopic mechanism able to account for the numerous experimental observations. A thorough overview of these efforts has been published in the introduction of a recent report [10]. There is now a general agreement that the observation of macroscopic oscillations in this system can be traced back to a local oscillation on the microscopic scale: silicon-oxidation/silicon-oxide-dissolution cycles take place at local "domains" (spots of limited spatial extension on the electrode surface, not necessarily located at fixed positions from cycle to cycle), and only can the synchronisation of these local current densities (current "bursts") over the surface give rise to a macroscopic current oscillation. These results pointed anodic dissolution of silicon in fluoride electrolytes as rather peculiar among other electrochemical oscillatory systems, in that the

oscillatory behaviour is present here on the microscopic scale, unlike the case of the vast majority of electrochemical oscillators, for which it is brought by a coupling on the macroscopic scale [1].

It has been soon recognized that in many occurrences the observation of self-sustained current oscillations under potentiostatic control arises from the presence of a series resistances in the circuit (electrolyte, silicon, back-contact) [11]. Accordingly, the intrinsic behaviour of the current in this system is actually a damped oscillation, which may be triggered by any perturbation in the applied potential. Such perturbations make the various regions of the surface phase-synchronised, and a macroscopic current oscillation is observed for a while, until the various self-oscillating "domains" lose their coherence, letting the system relax to the random situation. In this respect, it was stated that the intrinsic interface behaviour is better termed "resonant" rather than "oscillatory" [12,13]. This correspondence between a microscopic self-oscillation and a macroscopic resonant behaviour was put into a quantitative theoretical form assuming a stochastic desynchronising component only, i.e., independent non-interacting domains [12]. This work provided a detailed account of the very complex impedance diagrams observed in the resonant regime [13], and explained how a series resistance may turn the resonant behaviour into self-oscillating [11].

At this stage, the description of what is a self-oscillating domain is missing. In order to answer the question, two detailed microscopic models have been elaborated and tested using numerical simulations. They have been elaborated by the groups of Föll [10,14] and Lewerenz [6,15]. Both models describe the micro-oscillators as domains where fast oxide growth takes place during an active

* Corresponding author. Tel.: +33 169334663; fax: +33 169334799.
 E-mail address: jean-noel.chazalviel@polytechnique.fr (J.-N. Chazalviel).
 [1] ISE member.

time, and slow oxide dissolution takes place during an idle time. As outlined in the next section, they differ in the identification of the relevant non-linear, local microscopic mechanism which prevents the oxide thickness from reaching a steady state. Independently of the very nature of the microscopic mechanism, the existence and the nature of short-range coupling interactions between the micro-oscillators (predicted by the two models) raise open questions on the stability of the system. In particular, putting aside the trivial case of synchronisation by the series resistance of the circuit already mentioned, one may wonder whether the system always converges toward a steady-state constant current density, or whether for some values of the experimental parameters (pH, fluoride concentration, potential), it undergoes a bifurcation toward a system oscillating at the macroscopic scale by intrinsic phase-locking of the microscopic oscillators.

Synchronisation through phase-locking of large populations of interacting oscillators is a problem relevant for many physical, chemical, biological and social systems. It has been considered in detail in the literature, and one of the most successful approaches is the Kuramoto model, which proved to be adaptable to many contexts [16]. The Kuramoto model deals with the problem of phase oscillators submitted to mutual phase-dependent couplings that tend to synchronise them. As intuitively expected, it can be shown that, in many cases, the system can reach a stationary globally or partially synchronised state as soon as the synchronising coupling exceeds a critical strength. The main purpose of the present work is to address the existence of such a (at least partially) synchronised state in the case of the anodic dissolution of silicon in fluoride electrolytes, and to explore whether this state is reached or approached in appropriate experimental conditions. Unfortunately, using the usual Kuramoto formulation appears inappropriate in the present case because it implies a mean-field approximation, which exactly describes the trivial case of a global coupling such as that arising from series resistance, but short-range versions of the model do not appear amenable to analytic resolution, except for one dimensional systems [17]. We therefore used a simplified formulation of the problem which makes analytic predictions possible in addition to numerical simulations. In our approach, the strength of the synchronising coupling can be tuned at will, giving a unified framework for continuously going from the case where no interaction exists (previously considered in [12]) to that where its existence (envisioned by theoretical models of the silicon anodic dissolution in fluoride electrolytes) may yield experimentally observable consequences. However, before describing our model and comparing its quantitative predictions against experimental results, we will first shortly review how the current theoretical models of silicon anodic dissolution assume the existence of a synchronising coupling between the local micro-oscillators and introduce how the existence of such a coupling can be experimentally sought for.

2. Coupling interactions in existing models and in experiments

As already mentioned, two detailed microscopic models have been elaborated by the groups of Föll [10,14] and Lewerenz [15]. In the former so-called "current burst" model, the origin of the microscopic oscillation is electrical. Namely, it is assumed that the current through the interfacial oxide film is switched on when the electric field gets larger than some critical value, leading to fast increase of oxide thickness, and it is switched off when the electric field decreases below another (lower) critical value, these two threshold values being distributed with two distinct probability laws. In the latter model, to which the "current burst" term could be applied as well, the sudden increase in current density is triggered by stress-induced mechanical breakdown of the oxide film.

Both models include coupling interactions between the domains (unlike Ref. [12]) and are able to reproduce a number of the experimental findings, including for the resonant behaviour, though some observations (e.g., the detailed shape of the IR spectra [18]) appear hardly compatible with either of them. The synchronising interaction considered in Refs. [10,14] is a steric effect (two neighbouring domains tend to get phase-synchronised when the associated oxide islands overlap), whereas that considered in Ref. [15] originates from a stress effect (the time of oxide breakdown is affected by the stress induced by a neighbouring domain). Both of these interactions can be termed "short-range", in that the coupling strength decreases with distance more steeply than a Laplacian field (e.g., Coulomb or diffusion field [19]), and the effective coupling range is orders of magnitude smaller than the electrode size. Moreover, both of these models [10,14,15] invoke the need for a "desynchronising" interaction between neighbouring regions in order to avoid phase-synchronisation of the oscillation over the whole electrode surface.

However, the authors in Ref. [15] claim to account for the possibility of self-sustained oscillations, even in the absence of any series resistance. As a matter of fact, the two approaches indicate that the observation of an intrinsic, macroscopic self-oscillatory behaviour is still regarded as possible as a consequence of the presence of domain coupling. In the electrochemical literature, there are indeed numerous examples of domain synchronisation and pattern formation on electrodes, but this is associated with either "global coupling" through the uncompensated series resistance or "long-range coupling" through the distribution of potential or reactant concentrations in the electrolyte [19]. Here, we will simply investigate the point whether or not phase-synchronisation of the oscillation over a macroscopic electrode can be obtained through short-range interactions only. The presence of a macroscopic self-sustained oscillation could be regarded as the key test for evidencing the presence of a synchronisation interaction. However, this test is actually too strong, since one can imagine that a weak interaction may lead to a partially synchronised state of micro-oscillators, quite distinct from the random state, without yielding a macroscopic current oscillation [16,17]. A more sensitive test consists in observing the evolution of the system initially placed in a state where all the local oscillators are in phase: in the absence of any synchronising mechanism, the system would return to a random steady state through an exponential relaxation (damped current oscillations). The presence of a synchronising interaction is expected to affect the relaxation by lowering the damping rate, even if the macroscopic current density still converges toward a steady-state value. Interestingly, the experimental system can be prepared in an all-synchronised state by application of a potential perturbation triggering a current oscillation. This possibility provides us with an attractive tool for testing theoretical predictions against the experimental measurements.

Therefore, in the following, we will try to assess the competition between synchronisation and desynchronisation, without invoking a specific desynchronisation interaction, but just including a stochastic process (fluctuation of the local-oscillator period) on the microscopic scale. The synchronisation state over the surface will be measured through the root-mean square value of the distribution of the oscillator period on the electrode surface, and the relaxation of the system from an initial synchronised state will be calculated. These analytical predictions, checked by numerical simulations, will allow us to derive quantitative bounds for examining whether or not the existing experimental data on self-sustained oscillations have to call upon a global or a long-range interaction (typically, global coupling mediated by the series resistance of the electrolyte). We will not attempt to tell between the two conflicting models for silicon anodic dissolution in fluoride electrolytes because the coupling between oscillators is treated in our model in a general way compatible with the ingredients present in either