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Preliminary note

The p-Si/fluoride interface in the anodic region: damped and/or sustained oscillations

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The anodic dissolution of silicon in fluoride media has given rise to much excitement in recent years [1–10], particularly concerning the intriguing current oscillations sometimes observed in the anodic region (2.5 V $< E_{SCE} <$ 7 V). Several authors [1,5,10–12] have found that the current exhibits spontaneous oscillations above a critical potential $\approx$ 3 V_{SCE}. On the contrary, other authors [8,9] have found damped oscillations, which appear only upon a perturbation of the electrode potential. This has allowed them to perform a detailed investigation of the electrochemical impedance in that regime, and to propose a model accounting for their experimental results [9,13]. The origin of the discrepancy between the various authors was somewhat of a mystery. However, the compositions of the electrolytes were different in the various groups, and, interestingly, the electrolytes where sustained oscillations had been observed are in a fluoride concentration range higher than those where the damped ones had been reported. We will show here that, irrespective of the electrolyte composition in a wide fluoride concentration and pH range, the oscillations can be made intentionally damped or sustained, depending upon the value of the uncompensated resistance in series with the interface. All our experiments have been performed on low-doped p-Si electrodes (resistivity 1–4 Ω cm). We performed two kinds of experiments.

The first experiments demonstrate that, on a given interface, with damped oscillations ("steady" interface), a sustained oscillation can be created by adding an external resistor in series with the working electrode. We have taken the

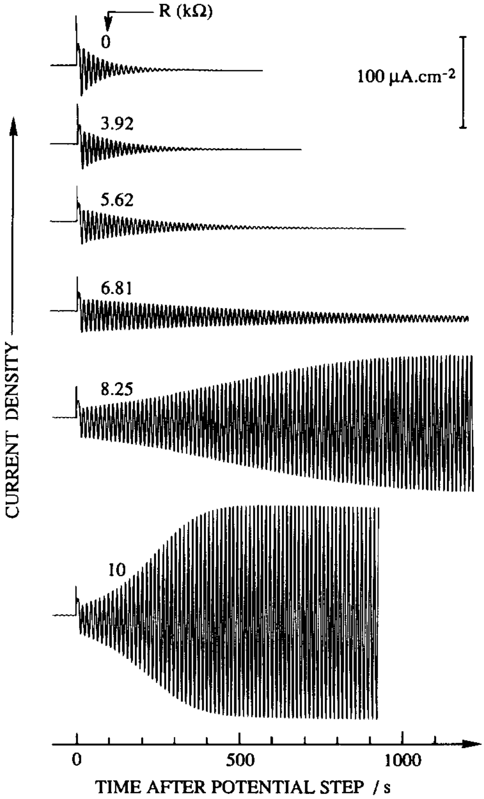

Fig. 1. Current transients observed in response to a +100 mV step-potential excitation, for an electrode with an externally added series resistor. The value of the added series resistance (kΩ) is indicated on the different curves. p-Si ($N_A = 2 \times 10^{15}$ cm^{-3}, (100) orientation, surface area 0.12 cm^2)/0.025 M HF+0.025 M NH_4F+0.95 M NH_4Cl, rotating disk electrode 300 r.p.m. Initial electrode potential is set at +3 V (corrected for the ohmic drop in the added series resistance). Notice the decreased damping rate, as the series resistance is increased, and the change to a sustained oscillation between 6.81 and 8.25 kΩ.

electrolyte 0.025 M HF + 0.025 M NH_4F + 0.95 M NH_4Cl (fluoride concentration $c_F = 0.05$ M, pH 3), well known for giving rise to damped oscillations with frequencies between 10^{-2} and 10^{-1} Hz [8,9]. A variable external resistor has been added in series with the working p-Si electrode. The damped or sustained character of the oscillations in this system has been tested in the following way: first a fixed potential was applied to the electrode (e.g. + 3 V_{SCE} in Fig. 1), then a stable current was obtained (i.e. no current oscillations), either by waiting for a sufficient length of time, or better by using an appropriate feedback, mimicking a negative capacitance in series with the interface [9] (this means that the applied potential must be increased when the current passes through its maximum, and

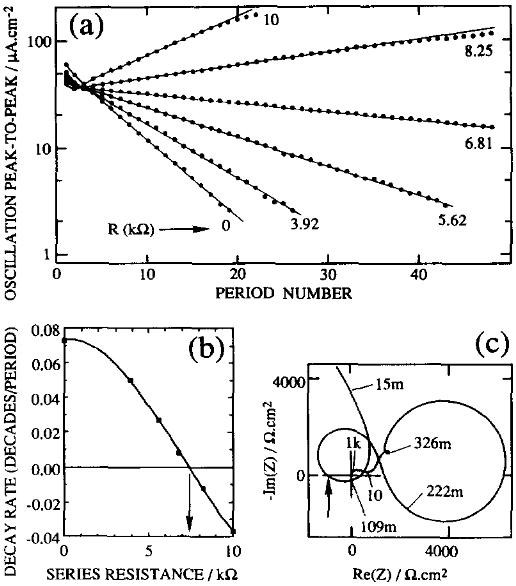

Fig. 2. (a) Semi-log plot of the data in Fig. 1. The amplitude decay is seen to be exponential. (b) Decay rate as deduced from (a). The change of sign (switching behaviour to a spontaneous oscillation) is seen to occur for a critical value of the series resistance $R_c \approx 7.5$ kΩ. (c) The impedance diagram (reproduced from ref. 9) is seen to exhibit a low-frequency loop with real-axis crossing at $-R_c$ (here $R_c = 900\ \Omega\ \mathrm{cm}^2/0.12\ \mathrm{cm}^2 = 7.5$ kΩ).

decreased when the current is minimum). Then at time $t = 0$, the feedback (if present) was removed, a small potential step was applied to the interface (+100 mV in Fig. 1), and the resulting current oscillations were observed. In all the cases represented in Fig. 1, the envelope of the oscillations is seen to be nicely exponential (see the semi-logarithmic plots in Fig. 2), but its characteristic decay rate is seen to decrease as one increases the value of the resistance in series with the Si working electrode. For the two largest values of the series resistance shown in Fig. 1, the decay rate even becomes negative. In other words, the oscillation is not damped any more; its amplitude increases exponentially up to a stable value, corresponding to the amplitude of a sustained oscillation. The critical value R_c of the series resistance corresponding to the change from the damped to the sustained regime can be determined by plotting the decay rate as a function of the series resistance. R_c is obtained as the abscissa corresponding to zero decay rate. The value obtained (7.5 kΩ in Fig. 2) can be examined by comparison with published impedance data [9], also reproduced in Fig. 2. When a resistance R is added in series with the interface, this just amounts to a translation of the impedance diagram along the real axis in the Nyquist plane ($Z \to Z + R$). The shift corresponding to the critical value $R_c = 7.5$ kΩ is seen to bring the low-frequency loop of the impedance diagram to the point where it just passes through zero. The

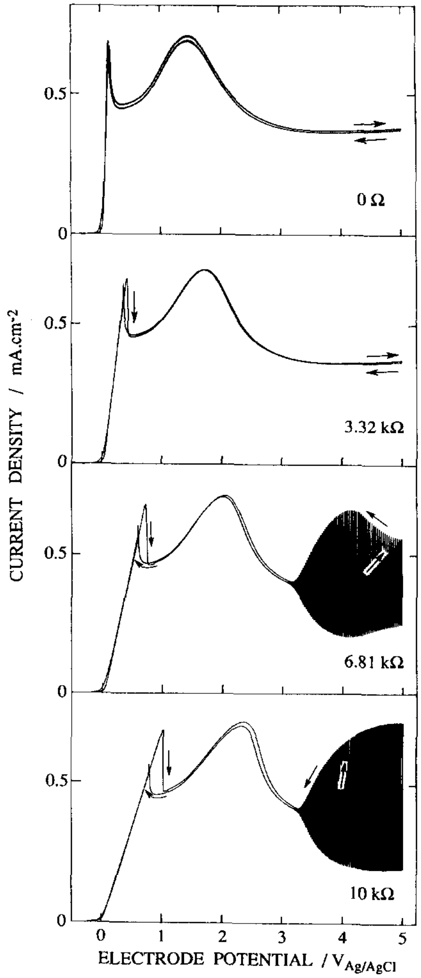

Fig. 3. Voltammograms of the same system as Fig. 1, with increasing values for the added series resistance R, indicated on the figure. Scan rate 2 mV s^{-1}. Notice that the large spontaneous oscillation appears on the forward scan, at about 4 V for the two higher values of R.

change from the damped regime to the sustained regime for this peculiar shift is just what one might have predicted from stability considerations on the impedance diagram [14].

Voltammograms for these systems are shown in Fig. 3. As previously mentioned [8,9], the interface normally exhibits oscillations on the backward scan only, because they are triggered by the sudden reversal of the potential sweep. The amplitude of these oscillations can be decreased at will by choosing a slower sweep rate, which was indeed done in Fig. 3. When a series resistance smaller than R_c is

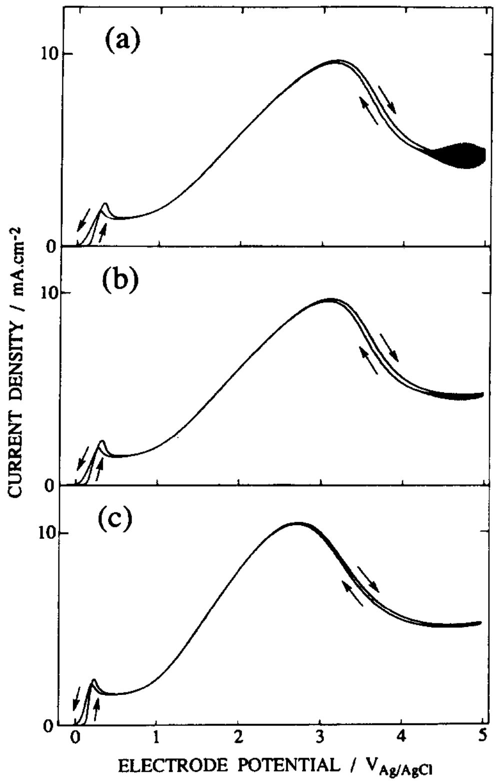

Fig. 4. Voltammograms for a system exhibiting a spontaneous oscillation: p-Si/0.165 M HF + 0.165 M NH_4F + 0.67 M NH_4Cl (c_F = 0.33 M, pH 3). Scan rate 60 mV s^{-1}. (a) Voltammogram in a typical cell. (b) As (a) but with the reference potential probed through a plastic-made Luggin capillary. The spontaneous oscillation has almost disappeared. (c) As (a) with electronic compensation of an 80 Ω series resistance. The spontaneous oscillation has been completely removed.

added, its effect on the general shape of the voltammogram is quite noticeable (see especially the region of the first current peak), but no significant change is seen in the region of the oscillations. When the resistance exceeds the critical value, large spontaneous oscillations appear on the forward as well as on the backward sweep. Interestingly, these oscillations are increasingly marked and similar on the forward and backward sweeps, as the sweep rate is made smaller: this comes just from the finite time needed to reach the steady-state oscillation amplitude, as seen from the last two recordings in Fig. 1. These experiments show unambiguously that, for this electrolyte, the damped oscillation can be made sustained just by adding a series resistance.

The second kind of experiment was aimed at checking whether a decrease of the series resistance is sufficient for removing the sustained oscillation when it is observed. Fig. 4(a) shows the voltammogram of a p-Si electrode in an electrolyte

($c_F = 0.33$ M, pH 3). A spontaneous oscillation, starting on the forward sweep, is quite discernible. This electrode was provided with low-resistance ohmic contacts (Au–Al evaporation at 600°C), so that electrolyte resistivity is thought to contribute significantly to the uncompensated series resistance. When the reference electrode is placed close to the working electrode, using a plastic-made Luggin capillary, the oscillations are seen to be almost (but not quite) suppressed (Fig. 4(b)). When electronic compensation for an 80 Ω series resistance is used, the spontaneous oscillations disappear completely, and only a very small damped oscillation, induced by sweep reversal, can be seen on the negative sweep. An independent test has been performed on an electrode provided with another type of ohmic contact (Ga–In eutectic) in a slightly different electrolyte ($c_F = 0.3$ M, NH_4FpH 3.5). In these conditions, it has been found that the interface does exhibit spontaneous current oscillations above a critical potential [10]. However, the ageing of the electrode for a few months (hence diffusion of the ohmic contact and lowering of the specific contact resistance) has been sufficient to induce the change from the sustained to the damped oscillation regime. This shows that cancellation or appropriate compensation for the resistances in series with the interface suppresses the sustained oscillation, bringing the system back to the damped oscillation regime, which then appears as the true intrinsic interface behaviour. Similar results have been obtained in a variety of different electrolytes representative of those already investigated in our different groups and hence appear to be quite general for the p-Si/fluoride–electrolyte interfaces. Our results demonstrate that the series resistances may originate either from the electrolyte, or from the electrode resistance and a non-ideal back-contact. The presence of such undesirable resistances is especially critical for electrolytes in the high fluoride concentration range, because increasing the fluoride concentration results in increasing the interface current and decreasing the characteristic impedances of the system; hence, the critical resistance R_c of Fig. 2 turns out to be lower and the criterion for crossover to the sustained oscillation regime is more readily reached with relatively small series resistances.

In conclusion, the p-Si/fluoride–electrolyte interface in the anodic regime can be switched between a damped and a sustained oscillation regime, just by changing the resistance in series with the interface. When the effective series resistance is zero, the damped oscillation regime is obtained, which then appears as the true intrinsic interface behaviour.

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