A Universal Topology in Nonlinear Electrochemical Systems

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In this paper we present an interesting universal topology occurring in different kinds of electrochemical oscillatory systems, namely, a crossing cycle in the cyclic voltammograms, which means there are a pair of overlapping negative and positive nonlinear feedbacks. The topology can provide with a simple intuition prediction as to whether or not an electrochemical system is possible to oscillate with an appropriate choice of parameters.

Nonlinear phenomena have been observed in a number of electrochemical processes since the first publication by Fechner[1] in 1828, including electrodesolution of metals, electrodeposition of metals, polarographic reduction, electrocatalytic oxidation of small organic molecules, and so on.[2-4] In fact, there are probably more examples of oscillating systems in electrochemistry than in any other area of chemistry.[3] Because electrochemical oscillations can be easily monitored by simple current, potential, or voltage control, and parametric changes of a few orders of magnitude can be easily applied to electrochemical systems, nonlinear electrochemical systems have been found to be most valuable as models for more complicated chemical or physiological nonlinear systems. For instance, it has been reported that the activity/passivity fronts appeared in anodized iron wires serve as a powerful model for information transfer in mammals,[5] and the electrochemical oxidation of formic acid shows stimulus-response behavior analogous to that of a nerve.[6]

It has been suggested[7] that electrochemical oscillations can be classified on the basis of impedance spectroscopy into two categories: the steady-state current-voltage curve exhibits (i) a negative slope with a negative impedance and (ii) a positive slope with a "hidden" negative impedance. Whereas, a negative impedance is not indispensable for electrochemical oscillations.[8]

An alternative classification of the electrochemical oscillations could be made from the viewpoint of electrode processes, since electrochemical oscillations can be generated by the coupling of electrochemical reactions (charge transfer) principally either with (i) mass transfer (diffusion, convection, and electric migration), or with (ii) surface steps (e.g., ad/desorption). The reductions of $S_2O_8^{2-}$, $Fe(CN)_6^{3-}$, IO_3^- on mercury[3] or solid electrodes,[9] and the electrodeposition[3] of Zn, Cd, Sn are all typical examples for the first category. Whereas the electrooxidation of CH_3OH, HCHO, HCOOH as well as the electrodesolution of Fe, Ni, Cu are typical examples[3] for the second category. Upon a constant stronger agitation, oscillations disappear for the first category,[9] but remain for the second category, which is a simple and efficient test method to distinguish the two categories of oscillations.

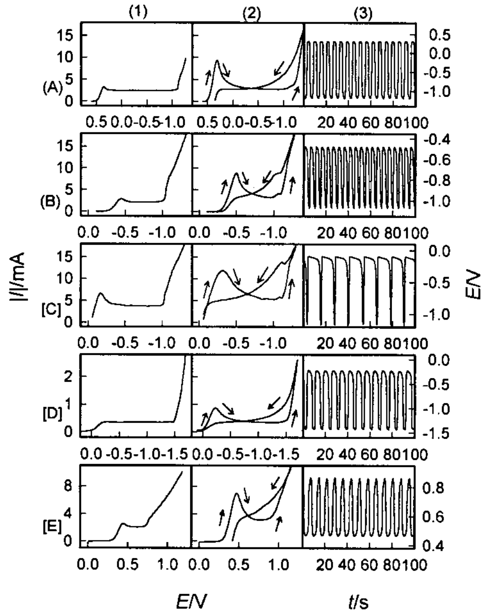

Figure 1. (1) Current-potential curves at 10 mV s^{-1}, (2) Cyclic voltammograms at 100 mV s^{-1}, and (3) Potential oscillations at (A) 4 mA, (B) 5 mA, (C) 6 mA, (D) 0.45 mA and (E) 3 mA, on a 3 mm diameter Pt disk except for (D) which is on a 1 mm diameter Ag disk, for the reduction of (A) 0.8 mol dm^{-3} $Fe(CN)_6^{3-}$, (B) 0.1 mol dm^{-3} IO_3^-, (C) 1 mol dm^{-3} H_2O_2, (D) 0.6 mol dm^{-3} $S_2O_8^{2-}$, and the oxidation of (E) 0.6 mol dm^{-3} $Fe(CN)_6^{4-}$ with 1 mol dm^{-3} NaOH as the supporting electrolyte. The potential is vs. Hg(l)| HgO(s)| 1 mol dm^{-3} NaOH. Room temperature.

The voltammograms for the electrochemical oscillatory systems mainly involving mass transfer (Figure 1) have typical geometrical structure or topology and can be explained straightforwards. As shown in Figure 1A for the cathodic reduction of $Fe(CN)_6^{3-}$, a limiting current plateau in the current-potential curve (column 1) implies that there is a bistability, i.e., $Fe(CN)_6^{3-}$ reduction only at the higher potential side of the plateau and hydrogen evolution with $Fe(CN)_6^{3-}$ reduction at the lower potential side of the plateau. A crossing cycle in the cyclic voltammogram (column 2), where the current value for the reverse scan is larger than that for the forward scan, means that there are two overlapping opposite processes between the bistable states concerning the variation of the reactant surface concentration, i.e., depletion (forward scan) and replenishment (reverse scan) of the $Fe(CN)_6^{3-}$ surface concentration by reduction under diffusion control and by convection induced through hydrogen evolution, respectively, and account for the potential oscillations (column 3). We call the depletion and replenishment processes negative and positive feedbacks. Similar phenomenon was also observed for the anodic oxidation of $Fe(CN)_6^{4-}$ (Figure 1E), in which oxygen evolution took place instead of hydrogen evolution.

However, only bistable states exist for systems with merely a limiting plateau without a crossing cycle as shown in Figure 2 B and C. In addition, when the crossing cycle is going to vanish with a dilute solution of $Fe(CN)_6^{3-}$ (Figure 2A), the $Fe(CN)_6^{3-}$ convection flow induced by the hydrogen evolution is too small

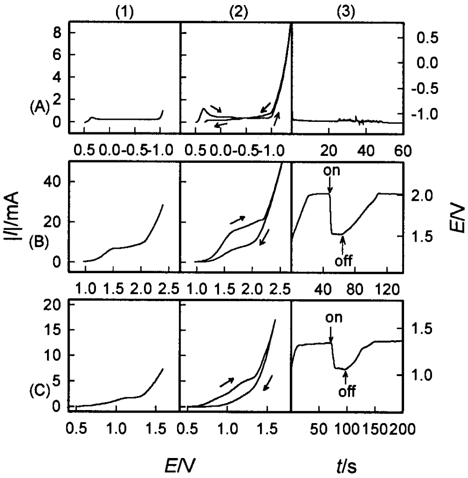

Figure 2. (1) Current-potential curves at 10 mV s^{-1}, (2) Cyclic voltammograms at 100 mV s^{-1}, and (3) Potential-time curves at (A) 1.5 mA, (B) 14 mA, (C) 3 mA on a 3 mm diameter Pt disk for the reduction of (A) 0.1 mol dm^{-3} $Fe(CN)_6^{3-}$, and the oxidation of (B) 0.6 mol dm^{-3} $S_2O_3^{2-}$ and (C) 0.6 mol dm^{-3} SO_3^{2-} with 1 mol dm^{-3} NaOH as the supporting electrolyte. The potential is vs. Hg(l)| HgO(s)| 1 mol dm^{-3} NaOH. Room temperature. "On" and "off" indicate when the agitation begins and stops, respectively, which is the method as used in Ref. 10 to show the bistability.

to repress the hydrogen evolution and restore the state with $Fe(CN)_6^{3-}$ reduction only, i.e., without a sufficient positive feedback, so only small noise appears and then the potential stabilizes at the lower potential side of the limiting current plateau. A constant stronger agitation can also stop the sustained oscillations in Figure 1 because no reactant depletion at the electrode surface can occur in this case, i.e., no effective negative feedback, and the potential remains at the left-hand side of the plateau. Thus the topology of a crossing cycle necessary for the oscillations has its definite physical meaning: overlapping negative and positive nonlinear feedbacks.

The topology of a crossing cycle, too, occurs in the electrochemical oscillatory systems mainly involving surface steps, such as in the electrocatalytic oxidation of small organic molecules and in the electrodesolution of some metals as shown in column (1) of Figure 3A and Figure 3B for systems of HCHO and Cu, respectively. The crossing cycle in the HCHO oxidation probably comes from the surface adsorption of CO_{ad} and its removal through reaction with the OH_{ad} as generally accepted, while in the Cu electrodesolution it may come from the surface film formation of CuCl(s) and its removal in the form of $CuCl_2^-$ (aq) or Cu^{2+} (aq).[11] We also give an example for current oscillations in Figure 3C, which appear exactly in the potential region where the current-potential curve exhibits a negative slope, which is similar with many polarographic reduction systems.[3] Again, a crossing cycle is present in that region for the cyclic voltammogram (column 1 of Figure 3C) with a very large reverse scan current value.

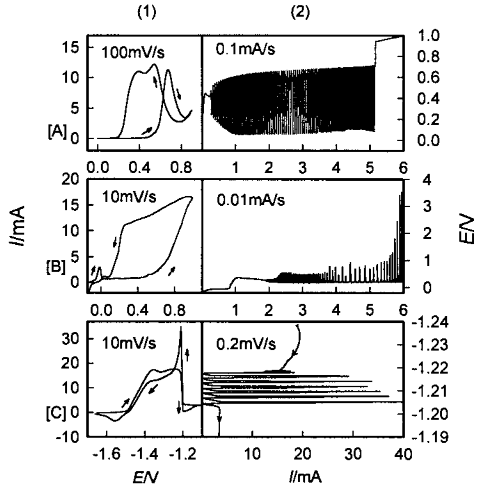

Figure 3. (1) Cyclic voltammograms, and (2) Potential or current oscillations for (A) 0.5 mol dm^{-3} HCHO oxidation in 1 mol dm^{-3} H_2SO_4 on a Pt wire of 1 mm in diameter and 8.5 mm in length, (B) 2.7 mm diameter Cu disk electrodesolution in a solution containing 0.5 mol dm^{-3} H_2SO_4 and 0.5 mol dm^{-3} KCl, (C) 3 mm diameter Zn disk electrodesolution in 5 mol dm^{-3} NaOH. The potential is vs. SCE. 30 ± 1 °C.

The role played by the external series resistance (R_e) required sometimes for current oscillations under constant voltage (U) control[12] is to supply another pair of negative and positive feedbacks. Because $U = E + IR_e$ holds while overlooking the resistance of solution or combining it into the R_e, the potential (E) in the cell will vary in opposite direction with the ohmic drop IR_e at a given U, i.e., a larger I reduces the E and thus the I itself; and vice versa. This pair of feedbacks from the resistance cooperate with those feedbacks from the chemical and /or physical processes of the oscillating system itself will intensify the unstable nature of the system,[9] which may be the reason why oscillations occur in a dilute solution during polarographic reduction.[4]

The meaningful topology is an essential summarization of the characteristics for different electrochemical oscillatory systems. It can act as a necessary condition for electrochemical oscillations and furnishes with a simplest way to predict and further realize electrochemical oscillations under appropriate parameter conditions.

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