

CHAPTER 7. SUMMARY AND OUTLOOK

The electrocatalysed oxidation of small organic molecules (mostly C_1 compounds) has seen a resurgence of interest in the search for suitable anodic reactions in devices for direct electrochemical energy conversion. Common to all reactions is the tendency towards self-poisoning of the reactive surface, mostly by carbon monoxide, and the existence of parallel reaction channels. Of all the striking features of the electrocatalytic oxidation reactions of organic C_1 fuels, their tendency to exhibit self-organised and spatiotemporal instabilities at higher overpotentials or current loads is perhaps the most remarkable. Thus bistability, oscillations as well as standing and travelling waves were obtained.

In Chapter 3, to assist in the basic understanding of electrocatalytic oxidation of C_1 molecules, CO oxidation on the Ru (0001) surface was investigated. In order to compare the electrocatalytic activity of rough Ru (0001) with that of a flat surface, cyclic voltammetry and current-time transient experiments were performed. Unlike the case of flat Ru (0001), a broader and featureless cyclic voltammetry (CV) curve was obtained on the rough surface. Three subsequent CVs on the flat Ru electrode are needed for complete oxidation of CO_{ad} , while on rough Ru, a single oxidation peak initiated at lower overpotential of +0.17 V gives rise to complete stripping of all CO_{ad} . Current-time transients at different electro-oxidation potentials indicated that a rough Ru (0001) surface could decrease the oxidation overpotential by *ca.* 550 mV compared with the flat surface. A comparable increase of activity of the rough surface was obtained in HCOOH oxidation. Summarising the experimental data, this reaction can be considered as a reference for the development of a more effective catalyst for CO tolerance in a hydrogen fuel cell.

Chapter 4 focused on nonlinear behaviour such as spontaneous oscillations of current or potential, complex and chaotic oscillations, associated bifurcation scenarios and spatial pattern formation, which occurs when the system is maintained far from thermodynamic equilibrium. The electrocatalytic oxidation of HCOOH on Bi/Pt ring

spontaneously underwent transitions from homogeneous catalytic activity to spatiotemporally inhomogeneous distributions of the interfacial electrode potential.

The pattern formation resulted from hybrid effects of the nonlinear chemistry during HCOOH oxidation and the long-range coupling of the interfacial potential, the form of which is determined by the chosen geometry (ring type) of the working electrode. With negative coupling conditions, the anti-phase dynamics (standing waves or pulses) could prevent complete poisoning of the electrode, since passivation at some point on the electrode would enhance the catalytic activity at a remote location. This generally results in a prolonged catalytic reactivity of the electrode compared with stationary operation conditions. Propagating pulses on the Pt ring were externally perturbed *via* a trigger electrode at one location of the ring. While usual phase resetting was obtained for small perturbation amplitudes, stronger perturbations resulted in reversal of the direction of pulse motion when applied behind the pulse over a wide phase interval.

Whether in-phase and anti-phase oscillations of the double layer potential were selected strongly depended on the reference electrode distance parameter β , which was defined as the ratio of the distance between the working electrode and the reference electrode to the outer radius of the ring-shaped working electrode. In-phase homogeneous oscillations were obtained at $\beta \geq 0.7$, due to the positive global coupling, while anti-phase inhomogeneous patterns in the form of travelling pulses were observed at $\beta \leq 0.25$, due to negative nonlocal coupling. Within an intermediate reference position range from $\beta \sim 0.70$ down to $\beta \sim 0.3$, there exist complex patterns and their theoretical interpretations are still unclear.

The mechanistic origin of electrochemical oscillations of HCOOH on Bi/Pt was discussed. Although CO formation is largely suppressed, a hidden negative differential resistance (HNDR), most likely due to metallic Bi, was identified from the electrochemical impedance spectra near the onset of potential oscillations, while a manifest NDR, probably due to adsorbed oxygen species, appeared to be responsible for the oscillations at higher overpotentials on the anodic scan in the electrocatalytic oxidation of HCOOH.

Chapter 5 dealt with experimental observations of edge effects on a Pt ribbon electrode in the electrocatalytic oxidation of HCOOH, predicted theoretically. The

spatiotemporal pattern formation under bistable and oscillatory conditions were investigated on pure Pt and on a Bi-modified Pt electrode, respectively. On a thin ribbon, pattern formation along the short axis can be neglected. Theoretical calculation by J. Christoph [27] predicted that there would be in-phase and anti-phase edge oscillations due to the positive and the negative long-distance coupling, respectively. This was clearly confirmed by experimental measurements; *i.e.*, inhomogeneous and homogeneous spatiotemporal patterns were observed at low and high β (β was defined as the ratio of the distance between WE and RE electrode to the length of ribbon WE).

Under bistable conditions, theory predicts that the local function of effective spatial conductivity diverges at the edges of the electrode. In other words, much smaller spatial resistance is observed at the two edges of the ribbon electrode, and experimentally it resulted in both higher migration current and higher double layer potential at the two edges compared with the centre.

In Chapter 6, experimental observations of the temporal dynamics in the electrocatalytic oxidation of methanol (CH_3OH) on pure and Ru-modified Pt electrodes were reported. Hidden negative differential resistance (HNDR) and instabilities of the system were investigated by means of an electrochemical impedance spectrum analysis, potential oscillations under galvanostatic control and current oscillations with the application of an appropriate external resistance. The Hopf bifurcation shifted to lower potential with Ru modification. On the ring, no spatial instabilities were obtained.

Many patterns observed in electrocatalysis have been well modelled and successfully proven by experiments. This could increase our understanding of spatiotemporal dynamics in many other systems where migration coupling plays a crucial role.

OUTLOOK

The interplay of chemical and electrical processes is a very widespread phenomenon in biological systems. In the following, an example is discussed how electrochemical studies (in particular edge effects) may improve the understanding of a biological problem.

Influence of edge effects on pulse propagation

Background: The speed at which an action potential travels an axon, called the conduction velocity, depends on a number of factors. One parameter of conduction velocity is the diameter of the axon. Velocity is proportional to the diameter of the axon: the greater the diameter, the faster the conduction. Another determinant is whether or not the axons are sheathed with myelin.

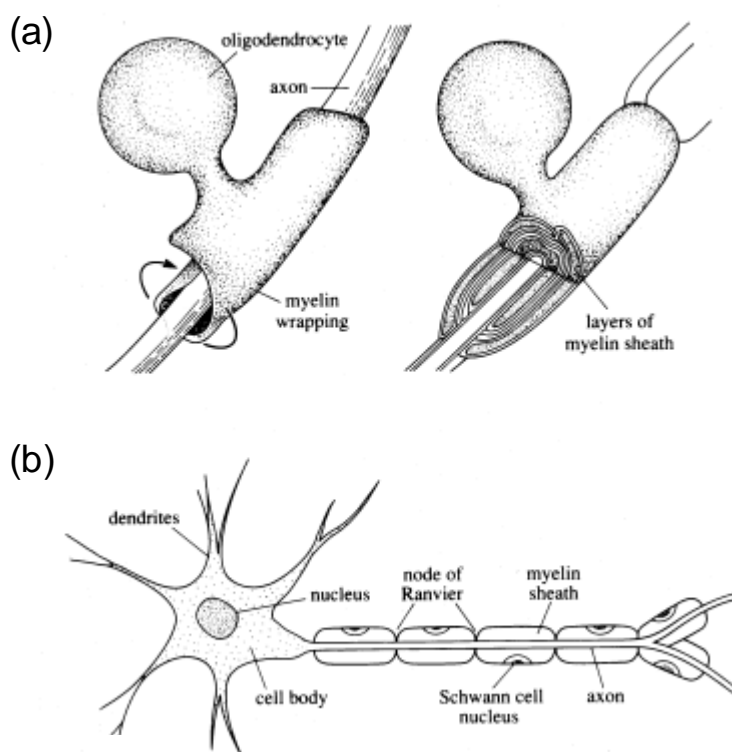


Figure 7.1. (a) An oligodendrocyte coats the axon membrane with a spiral sheath of myelin. (b) Nodes of Ranvier are gaps between successive myelin sheaths (after [188]).

In the peripheral nervous system, axons of sensory and motor neurons, and in the central nervous system, axons which connect relatively long distances between different brain regions are sheathed with myelin, an insulating fatty substance. Myelin presents a barrier to the exchange of ions between the inside and the outside of the membrane (see Figure 7.1).

In the peripheral nervous system the myelin is made by cells called Schwann cells, which wrap a myelin coating around the axon. In the central nervous system, myelin is provided by a different type of cell, called an oligodendrocyte. Examine Figure 7.1(b). Note that the axon is coated by myelin-providing cells which sheathe it with a spiral of myelin layers. There is a small gap between the successive myelin sheaths. The gap is termed a node of Ranvier. Nodes of Ranvier occur every 1–2 mm and are approximately $2\mu\text{m}$ in length (see Figure 7.2 for a schematic diagram of the nerve cell). The myelin sheaths and nodes of Ranvier play a crucial role in the propagation of an action potential, as described below.

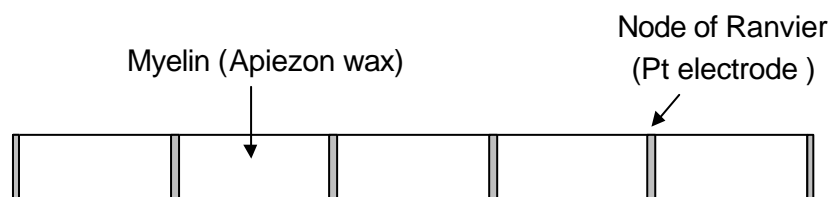


Figure 7.2. Schematic diagram of a ribbon electrode coated by Apiezon wax.

The propagation of an action potential along an unmyelinated axon is fundamentally the same as in a large number of continuous excitable media, from the BZ reaction to electrochemical pulses. The presence of myelin changes, in one important respect, the mode of transmission of the action potential. Despite their small sizes, the membrane patches exposed at the nodes of Ranvier have a high density of voltage-gated Na^+ channels. The action potential is unable to progress along the region of axon covered by the insulating myelin. Thus, instead of smoothly invading each successive patch of membrane as in unmyelinated axons, in myelinated axons action potentials jump from one node of Ranvier to the next. This significantly speeds up the conduction velocity compared with unmyelinated axons of the same diameter.

Present idea: Although the coupling is physically mediated by field effects (diffusion would be too slow), it is accepted that the travelling excitation pulses along unmyelinated nerve axons can be described by a continuous reaction-diffusion system (Hodgkin-Huxley theory). While discrete reaction-diffusion systems can exhibit a somewhat faster pulse velocity than continuous media, at least part of the acceleration may well be due to edge effects, *i.e.*, the divergence of the coupling function at the conductor/insulator (naked membrane/myelin) interface. Thus, the velocity of a pulse on an uncoated ribbon Pt electrode may be considerably smaller compared with the velocity on a ribbon Pt electrode coated by insulating Apiezon wax (see Figure 7.2).

Fuel cells

The variation of the phase shift between fluxes (current) and forces (potential) through periodic perturbations can lead to superior oscillatory operating conditions, enhancing the efficiency compared with that of stationary states. This idea has recently attracted renewed interest in the context of electrochemical energy conversion devices. Aside from temporal aspects, the control of spatial coupling across electrified interfaces may provide interesting applications. For example, electrochemical devices are conceivable where local activation of a poisoned electrocatalytic surface is sufficient to restore complete activity, if the interface supports propagating active fronts.

The three-electrodes setup with the counter electrode sufficiently far away from the working electrode was used in this work. However, there is no reference electrode in real fuel cells, and working and counter electrodes are often very close together in order to minimise ohmic losses in the electrolyte. In such cases, the coupling relevant for one electrode will not only depend on the potential distribution along itself, but also on the distribution at the other electrode. Thus, two types of migration coupling have to be considered, one along the electrode in question, the other between the electrodes. In this respect, further experiments and theoretical studies should be carried out.

