

Chapter 2

Basic Features During the Redox Transformation of CPs and the Coupled Phenomena

2.1 Electrochemical Perturbation, Leading to Phenomenological Changes

As it follows from the previous chapter, electrochemistry is the basic tool to control both the synthesis and especially the redox switching between the states: the isolator/conductor behavior can be tuned through the level of oxidation hence it regulates the number of the charge carriers. Generally, the electrochemical transformation of a CP between its nonconducting and conducting forms can be easily achieved by performing cyclic voltammetry in an adequately chosen potential range. Under optimal conditions (the details are beyond the content aimed in this book), the transformation is chemically reversible, meaning that the total charge during the cycle is zero: all the material oxidized during the positive scan is reduced on the reversed section. However, the voltammogram is to certify the lack of the electrochemical reversibility: the overall processes are more complicated than it follows from the simplified description in the introduction. During the oxidation half-cycle one broad current peak can be generally seen, but on the reduction side the overlapping of two peaks are revealed almost in all cases. It is also typical that at the anodic turnpoint the anodic current tends to reach a minimum nonzero level.

2.2 Color Change

The above-performed electrochemical transformation results in dramatic color changes: during the oxidation the excitation of the film becomes possible by lower energies, leading to a bathochromic transformation. These color changes typical for the actual family of CPs are perceptible to the naked eye, e.g., a cherry red–oxford blue transformation is easily noticeable for polythiophenes.

2.3 Mass Change

During the electrochemical transformations, the charge of the polymer backbone is changing. During the oxidation, the electron withdrawal creates excess positive charges. As a consequence of the electroneutrality rule, charge compensation through ion exchange with the adjacent solution should occur. This process is called improperly *doping* for virtual similarities in the conductance increase of inorganic semiconductors related to the presence of dopant, although there the cause and the consequence are just opposite.

Theoretically, there are two possibilities for the charge compensation process, due primarily to the relative ion mobilities within the channels of the given film. For the oxidative transformation of the polymer, the most evident consequence is the uptake of anions, which causes a mass increase. In other cases the electrochemically generated positive charges along the polymer chains expel cations from the film, and its mass is decreasing. Evidently, this may happen only when cations were already present in the CP in its neutral form, i.e., this layer contains a certain amount of both positive and negative ions with equal total charges. In several cases, when the mobility of the different ions is comparable, the motion of both ions can be revealed, and two distinct or overlapping sections in the mass change can be distinguished. During the discharging process the movement of the ions is opposite, and during a reversible redox cycle, the original mass of the film is regained. However, cycling the film in a solution containing other ions than those which were present during the electropolymerization process, the ion content of the layer can be modified. In that sense, we can distinguish CPs with anion or cation exchanger properties.

In special cases when some part of the polymer is able to dissociate, the so-called self-doping occurs via deprotonation (e.g., carboxyl derivatives). The removal of protons may take place also during the vigorous oxidation (from emeraldine base to pernigraniline) of polyaniline. The self-doping connected to proton movements causes small mass changes, generally close to the sensitivity limit of the measurement.

2.4 Conductance Change

A phenomenologic effect of the conductivity change manifests in polymer-based transistors which are already on the market. An organic field-effect transistor (OFET) uses an organic semiconductor in its channel. The most commonly used device geometry is bottom gate with top drain and source electrodes similar to the thin-film silicon transistor. The source and drain electrodes are directly deposited onto the thin layer of semiconductor, then a thin film of insulator is deposited between the semiconductor and the metal gate contact. If there is zero bias, there is

no carrier movement between the source and drain. When a proper oxidation potential is applied, a highly conductive channel forms at the interface.

Such a configuration can be used as an organic light-emitting device (OLET). The device structure comprises interdigitated gold source and drain electrodes, Positive (holes) as well as negative charges (electrons) are injected from the gold contacts into this layer leading to electroluminescence.

2.5 Diamagnetic/Paramagnetic Changes

Since the first product of the electrochemical oxidation, when one electron from the aromatic ring system has been withdrawn, is the monocation/polaron which is a cation radical, its paramagnetic pattern can be detected by ESR technique. When dications or bipolarons are formed, these species—possessing no unpaired electron—are not ESR active any more. Thus modification in the ESR signal during the electrochemical perturbation offers excellent tracing of the amount of intermediates. Although phenomenological consequence of the appearance/disappearance of paramagnetic species cannot be revealed, a special instrumental *in situ* technique—as it will be discussed in the Sect. 3.1—is a valuable tool for the discovery of the details.

2.6 Volume Changes

Since “doping” ions move together with their solvation sphere, ion incorporation may lead to the accumulation/depletion of the solvent in the channels, leading to swelling or shrinking of the surface layer. The process depends not only on the solvation properties of the ions, but considerably also from the wetting characteristics of the polymer in the actual solution. This phenomenon can result in bending of bilayer films of different solvophobic character, which motivated researchers to create artificial muscles.

2.7 Structural Changes

Incorporation or removal of ions (charged) and molecules (neutral) components has an effect other than simple swelling or shrinking of the layer: during a cyclic voltammetric process there is a continuously changing charge distribution within the film, which alters its polarizability, and—if it takes place in a modulated electric field—it manifests in structural changes connected also to the change in the dielectric/capacitive properties. Structural changes are connected to alteration in the extension of coplanarity along the polymeric backbone.

2.8 Transport Processes in the Adjacent Solution Layer

Income or outcome of the charge compensating ions results in concentration changes in the solution phase adjacent to the film, which in turns manifest in modification in the refractive index of this thin solution layer. Although this effect invisible to the naked eye, it can be visualized by special optical instrumentation (see Sect. 3.1).

The complexity of the phenomena related to the electroactivity of conducting polymers establishes their potential and already even realized applications. The importance of the field can be well illustrated by the fact that the 2000 year Nobel Prize in Chemistry has been awarded to Hideki Shirakawa, Alan MacDiarmid and Alan Heeger for the discovery and development of conductive polymers.

A special issue of the *Synthetic Metals* has been dedicated to the Nobel Laurates on the occasion of awarding [1].

Comprehensive overviews of these materials and their properties have been given in the multiple editions of the *Handbook of conducting polymers* [2–4], as well as in a later monograph [5].

References

1. Mele G, Epstein A (2001) Foreword. *Synth met* 125:1-1. doi:[10.1016/S0379-6779\(01\)00506-9](https://doi.org/10.1016/S0379-6779(01)00506-9)
2. Skotheim TA (ed) (1986) *Handbook of conducting polymers*. Dekker, New York
3. Skotheim TA, Elsenbaumer RL, Reynolds (eds) (1997) *Handbook of conducting polymers*. Dekker, New York-Basel
4. Skotheim TA, Reynolds (eds) (2007) *Handbook of conducting polymers*. CRC Press, London-New york
5. Inzelt G (2008, 2012) *Conducting polymers*. In: Scholz F (ed) *A new era in electrochemistry*, Springer, Berlin

In situ Combined Electrochemical Techniques for
Conducting Polymers

Visy, C.

2017, XI, 68 p., Softcover

ISBN: 978-3-319-53513-5