

APPLICATION NOTE

IN SITU UV–VIS–NIR SPECTRO- ELECTROCHEMISTRY ON ELECTROCHROMIC MATERIALS

By IFW - Dresden



METHOD

UV-VIS-NIR SPECTROELECTROCHEMISTRY

UV-vis-NIR spectroelectrochemistry is a combination of cyclic voltammetry (CV) and absorption spectroscopy in ultraviolet, visible and near infrared regions of the electromagnetic spectrum. Electron transfer reactions at electrodes results in the changes of the electronic structure of the electroactive species. These changes and their influence on the spectroscopic response of the compounds form the background of any spectroelectrochemical method. Thus, coupling cyclic voltammetry measurement with measurement of absorption spectra can give valuable information on the mechanism of the electrochemical reactions, the types of the formed charged species and their electronic structure. The in situ spectroelectrochemical method enables sensitive spectroscopic measurements under electron transfer conditions. Due to the accurate technique, the formation of charged species and evolution of their concentration in dependence on applied potential can be followed. UV-vis-NIR spectroelectrochemistry is the method of choice to study the redox processes in electrochromic materials. These materials can reversible change their color as a result of an electrochemical reaction and are an essential component in all kinds of electrochromic devices (ECDs). For the development and production of tailored ECDs, it is important to understand the mechanisms of the electron transfer reactions in such materials and to identify the species which are responsible for the coloration.

Applications of UV-vis-NIR spectroelectrochemistry to study on electrochromic materials:

- Real-time monitoring of electrochromic changes by redox reaction
- Spectroscopic detection and identifying the species responsible for the coloration
- Study of the optical properties and stability of charged species
- Concentration profile of (colored) species in dependence on stepwise varying potential
- Elucidation of the mechanisms of electrochemical reactions

INSTRUMENTATION

The spectroelectrochemical setup consists of a spectrometer, light source, potentiostat, fiber-optic cables and a spectroelectrochemical cell. It can be extended to other spectroscopic modalities, e.g. electron spin (paramagnetic) resonance (ESR/EPR) spectroscopy.

OUR SETUP:

AvaSpec Multi-channel System:

Needed to perform precise measurements over broad spectral range (200–2500 nm). Each spectrometer can be configured independently. The whole spectrum is measured at once in milliseconds.

AvaLight-DH-S-BAL:

A balanced deuterium and halogen light source, in which the alpha peak at 656 nm is significantly reduced. An integrated TTL-shutter can be triggered by the potentiostat.

Potentiostat:

Any potentiostat that provides TTL trigger outputs can be used for triggering the spectrometer. The Digital Input/Outputs (DIO) offers the possibility to synchronize electrochemical measurements with external devices controlled by TTL signals. To trigger an acquisition of the spectra on the spectrometer and control the shutter of the light source, a dedicated trigger cable is required. This cable is used to connect the EXTERNAL I/O connector located on the back of the spectrometer to an available DIO ports on the potentiostat. The acquisition of a spectrum is triggered by sending a TTL pulse from the potentiostat to the spectrometer and light source. Each pulse triggers the acquisition of one spectrum.

Bi- or multi-furcated fiber-optic cables:

Splitted out from the light sources to the cell and from the cell to the individual detectors. UV/VIS (250–800 nm) and VIS/NIR (350–2500 nm) fibers with different OH content are used.

Optically transparent thin layer electrochemical cell:

Needed to couple electrochemistry and absorption spectroscopy in transmission mode. Usually, noble metal meshes or substrates coated with indium-tin oxide or ultrathin layer of noble metal are used as working electrodes. Under thin layer conditions, a complete electrolysis of electroactive reactants is rapidly achieved. The interfering reactant absorption is minimized. This is more important in the case of consecutive electron transfer reactions. Cells with optical path lengths of 1.0, 0.5 or <0.2 mm are available and suited to techniques with simultaneous spectroscopic characterization of reaction products under finite and semi-infinite diffusion conditions.

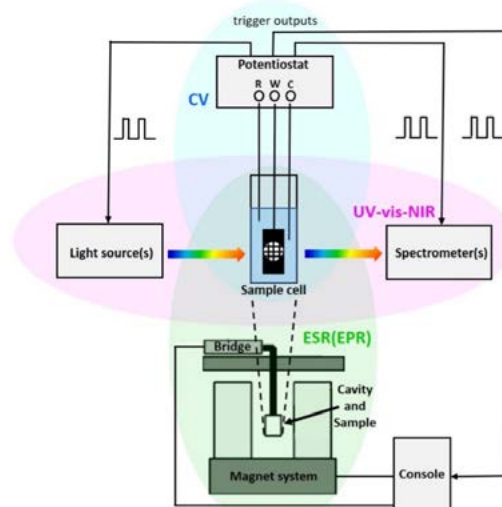


FIGURE 1
Spectroelectrochemical setup

STUDY ON VIOLOGEN SYSTEMS

Viologens (1,1'-disubstituted-4,4'-bipyridinium salts) are widely established as organic electrochromic compounds. The three common redox forms of viologens are the usually colorless dication, the highly colored radical cation, and the di-reduced (neutral) form. The radical cation and neutral form are generated by two consecutive reductions. The Spectroelectrochemistry group at the Leibniz Institute for Solid State and Materials Research (Germany) headed by Dr. Evgenia Dmitrieva, together with the CIDETEC Technology Centre (Spain) studied a series of viologen compounds by in situ UV-vis-NIR spectroelectrochemistry (Fig. 2).^{1,2} The electrochromic properties of the viologen systems can be modulated by varying the molecular structure of the viologens (substituents at the nitrogen atoms) and also by changing their environment (electrolytic media). ECDs based on symmetric compounds ($R = R'$) with alkyl substituents show violet coloration, while viologens with aryl groups demonstrate green coloration for their first reduced form (radical cation). ECDs based on asymmetric viologens ($R \neq R'$) may provide more neutral (greyish) coloration³.

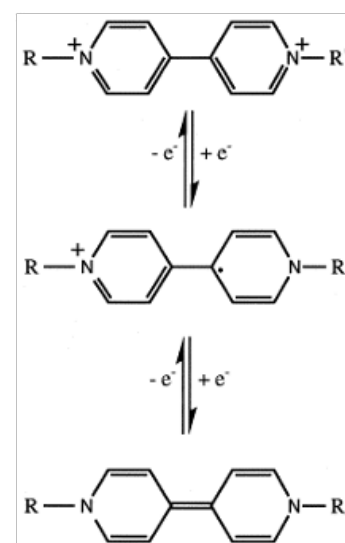


FIGURE 2

Three common viologen redox forms
R, R' = alkyl or aryl group

EDCs containing anhydrous organic solvent (propylene carbonate) and polyvinyl alcohol (PVA) – borax hydrogel as a polyelectrolyte demonstrate a different coloration. UV-vis-NIR spectra measured in PVA-borax gel during the reduction of ethyl viologen are shown in Fig. 3b and c on the next page. The analysis of the absorption spectra reveals three distinct patterns corresponding to the radical cation ($V^{\bullet+}$) and π -dimer ($(V^{\bullet+})_2$) formed during the one-electron reduction. Di-reduced structures are observed during the two-electron reduction (Table 1 on next page). The dimers are characterized by the bands which are blue-shifted compared to that of the radical cation and a pronounced charge-transfer band in the near infrared region. During the one-electron reduction ECDs provide a violet coloration in consequence of the absorption at 595 (blue radical cation) and 550 (purple π -dimer) nm (Fig. 3c, inset). Based on the spectroscopic data, it can be concluded that a large amount of the π -dimers are formed in PVA-borax gel and they significantly contribute to the color observation. In contrast to the polyelectrolyte, in polar organic solvents such as propylene carbonate no dimers are formed because ion pair formation precludes dimerization. In this case the device coloration is only caused by the absorption of the radical cation (Fig. 3d, inset). As summary, UV-vis-NIR spectroelectrochemistry on electrochromic compounds provides information about what kind of charged species are formed during the electrochemical treatment as well as their optical properties depending on experimental conditions.

TABLE 1

Electrolytic medium	UV-vis-NIR bands ($\lambda_{\max}$, nm)		
	radical cation ($V^{\bullet+}$)	dimer ($V^{\bullet+}$) ₂	neutral form
PVA-borax gel	395, 595 , 660, 731	365, 550 , 875	395, 470
propylene carbonate	397, 556, 606 , 662, 736	—	373, 397

TABLE 1

Assignment of the UV-vis-NIR absorption bands observed during reduction of EtV^{2+} . The dominant bands in the visible range are shown in bold.

FIG. 3A, B, C & D

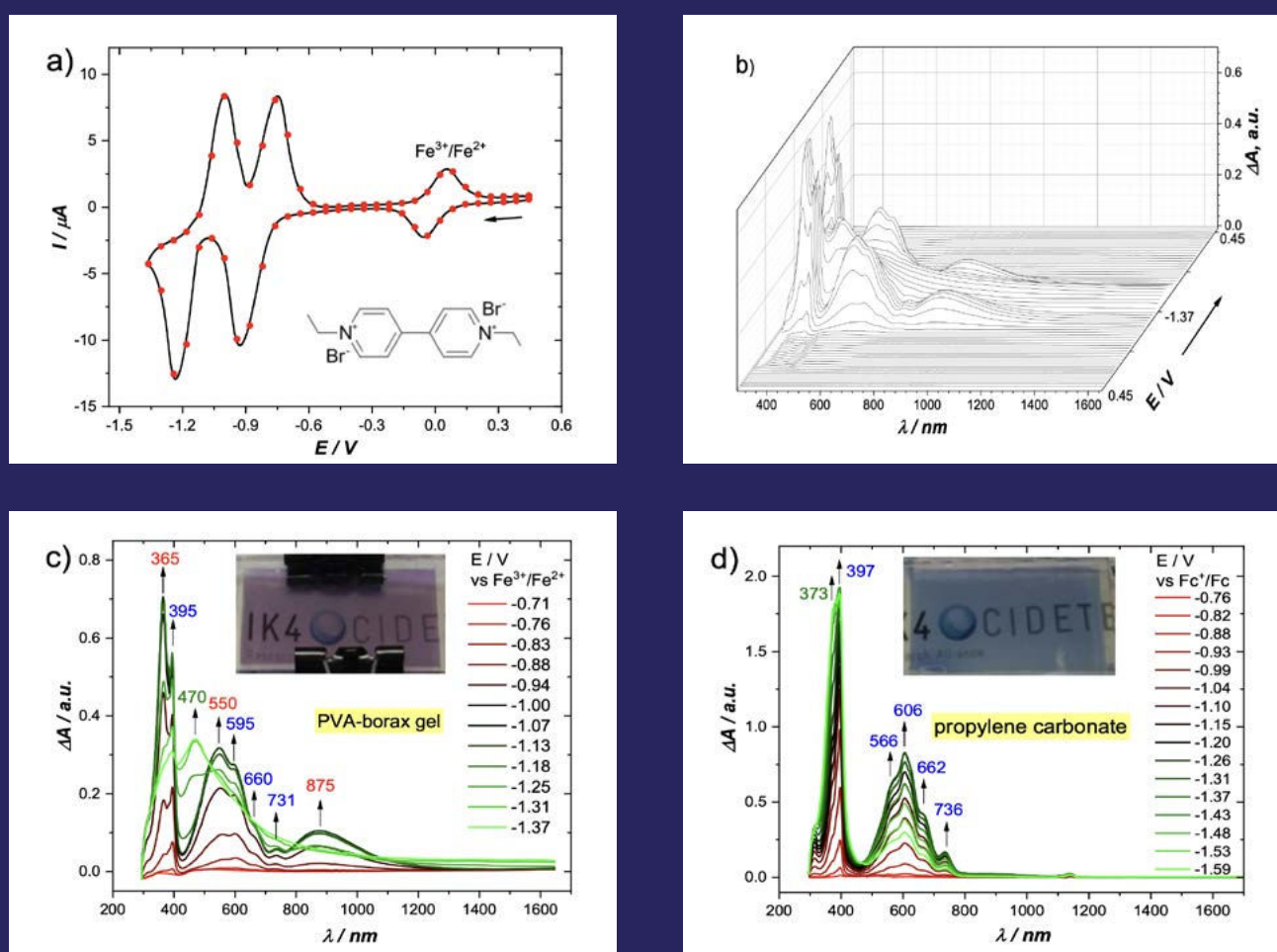


FIG. 3A, B, C & D

Cyclic voltammogram of ethyl viologen EtV^{2+} (Fig 3A) and 3D plot of the UV-vis-NIR spectra (Fig 3B) measured in PVA-borax gel during the reduction of EtV^{2+} . Potentials at which the spectra were measured are marked by red points. 2D plot of the UV-vis-NIR spectra recorded in PVA-borax gel (Fig 3C) and propylene carbonate containing 0.2 M TBABF₄ (Fig 3D). The spectrum of the solution containing 3.5 mM EtV^{2+} recorded at initial potential was taken as a reference spectrum. Inset: photographs of the device containing PVA-borax gel and propylene carbonate provide the coloration obtained during one-electron reduction.

COMBINATION ESR SPECTROSCOPY

The electron spin (paramagnetic) resonance (ESR/EPR) spectroscopy is the method of choice for detection and characterisation of structures containing unpaired electrons (e.g. organic radicals, transition metal ions). A primary step of the electron transfer in a neutral organic molecule leads to the formation of a radical ion, which can be unambiguously confirmed by ESR spectroscopy. A second electron transfer usually results in diamagnetic structures. UV–vis–NIR spectroscopy delivers information about the optical properties of both paramagnetic and diamagnetic species.

Polyelectrolyte-based ECDs containing p-cyanophenyl viologen and PVA-borax gel provide two different well-defined colored states (Fig. 4a). The application of the less negative potential leads to the observation of a green coloration, while the more negative applied potential generates a red one. By using the triple method (combination of cyclic voltammetry, electron spin resonance and electronic absorption spectroscopy) it is possible to identify the species responsible for each coloration. The dependence of the ESR signal and charge-transfer band intensities on applied potential demonstrates the evolution of the concentration of the radical cation and the dimer (Fig. 4b). The dominant species can be determined at stepwise varying potential. As result, a complete mechanism of viologen reduction can be elucidated.

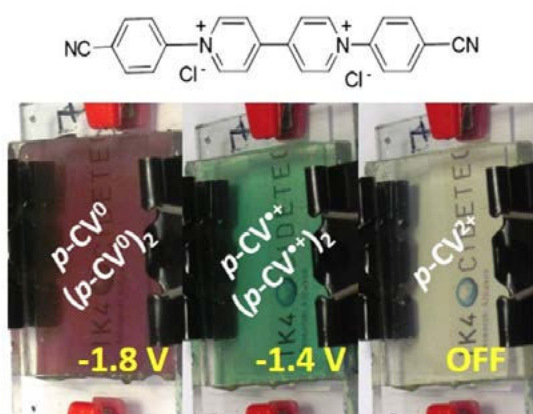


FIGURE 4A

A: Photographs of the device based on p-cyanophenyl viologen p-CNV²⁺ and PVA-borax gel at different applied voltage. The species responsible for the device coloration are indicated.

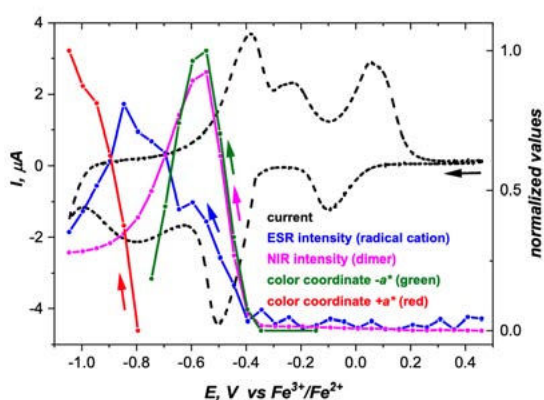


FIGURE 4B

B: Potential profiles of the ESR signal and NIR band intensities as well as color coordinates.

ABOUT IFW

[IFW](#) is a research institute where scientists and engineers work together and explore the physics and chemistry of materials that might be suitable for new functionalities. Many disciplines come together: experimental physics, theoretical solid-state physics, chemistry, materials research and electrical engineering.

What does IFW do?

Materials play an important role in technical progress in our society. New fundamental discoveries in physics or chemistry lead to the search for substances in which these new physical or chemical effects occur. Manufacturing processes, new devices and products need to be developed so these new effects can be exploited. It has always been like this; already in the Stone Age, when the hardness of stone was used for tools. Nowadays, we need materials for storing and transmitting information, filtering waves of a particular frequency, shielding a magnetic field or storing energy. These processes take place at the level of molecules, atoms and electrons. Scientists at IFW Dresden explore these physical fundamentals. We develop materials that have completely new functions or can perform better. Some examples: flexible magnetic sensors, materials that conduct electricity without resistance, biocompatible alloys, magnets that can cool their environment or substances that convert heat into electricity.

SOURCES

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