Anodic oxidation of dimethyl sulfoxide based electrolyte solutions: an *in situ* FTIR study

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Anodic oxidation of dimethyl sulfoxide (DMSO) based electrolyte solutions, containing $LiClO_4$, $LiBF_4$ and KPF_6, on platinum (Pt), glassy carbon (GC) and n-TiO_2 (anatase), electrodes was studied using *in situ* Fourier transform infrared spectroscopy (FTIR). All solutions contained small amounts of H_2O. Regardless of the supporting electrolyte all systems were unstable at potentials above 1.0 V vs SCE. The major oxidation product is dimethyl sulfone, formation of which is initiated by the trace water breakdown. In contrast to acetonitrile based solutions there is no evidence of electrolyte involvement in the breakdown process. Photoanodic decomposition of dimethyl sulfoxide based solutions proceeds in the same way as the anodic oxidation in the dark. In the presence of nucleophilic agent (iodides) the prevailing redox process is iodide oxidation. Small amounts of, probably, methylsulfinyliodide are also formed. The irreversible consumption of charge mediator significantly restricts the possible practical use of DMSO in photoelectrochemical devices.

1. Introduction

Research on lithium batteries [1] and photoelectrochemical cells [2, 3] has demonstrated the importance of suitable electrolyte/solvent selection. Thermodynamic or at least kinetic stability of the solvent/electrolyte system over a wide potential range is one of the basic properties governing a number of practically important parameters such as overcharging stability of lithium batteries or photoanodic degradation processes in solar cells employing n-type semiconductor electrodes.

Dimethyl sulfoxide (DMSO) is one of the most common aprotic solvents [4, 5]. It is a good solvent for many inorganic as well as organic compounds due to its high dielectric constant ($\epsilon = 47$) [6]. DMSO is particularly stable in the cathodic region and fairly stable in the anodic region. It reacts with alkali metals except lithium [4]. The limiting potential in the cathodic region varies both with the electrode material and the supporting electrolyte from -3.0 V (tetrabutylammonium perchlorate, Hg cathode) [7] to -1.8 V (sodium nitrate, Hg cathode) [8]. The nature of the cathodic limiting reaction in NaCl/DMSO solutions was studied by Giordano *et al.* [9]. The solvent decomposition is initiated by the reaction of metallic sodium with DMSO at the cathode. Hydrogen and a mixture of methane, ethane and ethylene are the main products of cathodic reduction. The ratio of hydrogen to hydrocarbons is a function of the current density [9].

On the other hand, the electrochemical oxidation of DMSO has not been studied as intensively and more specific data concerning anodic limiting reactions are lacking. The anodic limiting potential for the

DMSO/$LiClO_4$ system on a platinum anode was reported as 1.3 V vs SCE [5]. Electrochemical behaviour of dimethyl sulfoxide in H_2SO_4 aqueous solutions was studied by Alekseeva *et al.* [10]. They observed very strong adsorption of DMSO on platinum but there was no evidence of any decomposition process at potentials below oxygen evolution [10]. Chemical oxidation of DMSO was discussed in several papers [11–13]. Dimethyl sulfone was found as the major product of the oxidation of DMSO with KO_2 [11], potassium ferrate(vi) [12] or SO_4^{2-} radical [13]. In this paper we present the results of an *in situ* FTIR spectroscopy measurement of anodic (photoanodic) oxidation of DMSO based solutions with a view to its possible practical exploitation (e.g., in photoelectrochemical cells).

2. Experimental details

Dimethyl sulfoxide (Lachema, p.a.) was vacuum distilled and the fraction 75–80 °C (800 Pa) was collected. $LiClO_4$ and $LiBF_4$ and KPF_6 (Fluka, p.a.) were used as received. The 0.5 M electrolyte solutions were prepared in an argon-filled glove box (water content in the box atmosphere was lower than 20 ppm) and dried over 0.4 nm molecular sieves. Water concentrations are indicated in figure captions.

Electrochemical measurements were performed in a sealed, single-compartment cell using a platinum working electrode (projected area $A = 0.2\,\mathrm{cm}^2$), platinum auxiliary electrode and a saturated calomel electrode (SCE) reference electrode. A conventional three-electrode potentiostat was used.

Electrochemical *in situ* Fourier transform infrared spectroscopy (FTIR) experiments were performed

on a Nicolet 205 spectrometer equipped with a home-made accessory for specular reflection [14, 15]. Due to the use of the CaF_2 optical windows the $\lambda > 10\,\mu m$ radiation was cut-off. The anodic breakdown of DMSO was studied using platinum (diam. 10 mm) and glassy carbon (diam. 8 mm) working electrodes [15]. Photoanodic processes were studied on a n-TiO_2 (anatase) electrode prepared according to [16]. Photoexcitation of the working electrode was carried out by a 500 W high pressure xenon lamp. The light beam passed through a series of filters cutting-off the $\lambda > 350$ nm radiation. The total ($\lambda < 350$ nm) light power impinging on the cell window was $5\,mW\,cm^{-2}$ (as measured by a thermopile sensor, Coherent Labmaster, USA). In all spectroelectro-chemical experiments an Ag pseudoreference elec-trode was used. Its potential was between 200 and 250 mV vs SCE. Potentials were then recalculated and are quoted vs SCE. The sample compartment of the spectrometer was continuously purged with dry air purified also from CO_2.

I.r. spectra were recorded in a single beam reflectance mode with $4\,cm^{-1}$ resolution using the experimental procedure described in [14, 15]. Final reflectance spectra were obtained by averaging of 70 co-added spectral scans. The working electrode was held at 0.3 V at the so called 'base' potential for two hours before each series of spectral measurements to attain a constant composition of the gas phase in the spectrometer and sample compartment and a steady hydrodynamic state in the thin layer cell. The corresponding spectrum is denoted as the 'base spec-trum, R_0'. Subsequently, the potential was stepped from the base potential to 1.2, 1.7 and 2.0 V, respec-tively. The corresponding reflectance spectra, R, were measured at the sample potentials by the same way as the base spectrum, R_0. The reflectance spectra were recorded after 5 min exposition to the applied potential. The normalized difference, $(R - R_0)/R_0 = \Delta R/R_0$ was evaluated. This technique is similar to the so called Subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) method [17–19].

Measurements on a n-TiO_2 electrode were per-formed as described in [14]. Measured data were pro-cessed as described above. In this case, the 'base spectrum R_0' corresponds to the state of the electrode at a given potential in the dark. The reflectance spec-tra, R, refer to the electrode at the same potential after illumination. All infrared spectra are, accordingly, presented in the usual form where an increase in the concentration of infrared absorbing species in the optical path produces downwards extending peaks and vice versa [14, 15, 17–19].

The H_2O content in the solutions was measured with a WTK 901 Karl-Fischer coulometer (Direct, CR) before each spectroelectrochemical experiment. GC–MS analysis was performed on a Hewlett-Packard 5890/II gas chromatograph equipped with a 5971 mass spectrometer and a FID detector.
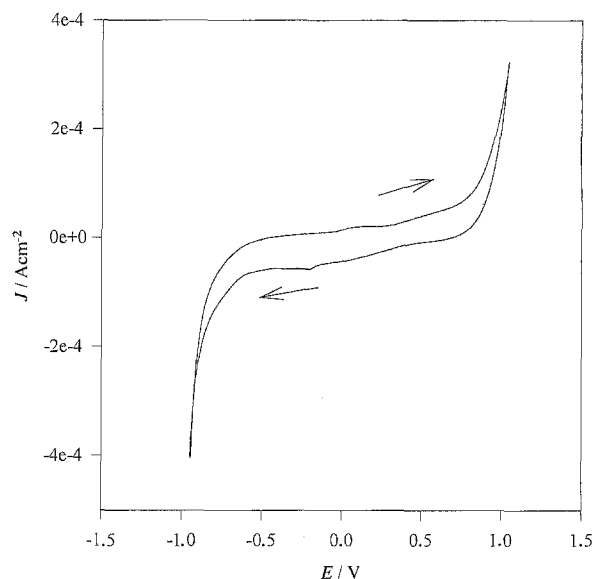

Fig. 1. Cyclic voltammogram of 0.5 M $LiClO_4$/DMSO system (0.04 M H_2O) on the Pt electrode ($A = 0.2\,cm^2$). Scan rate $100\,mV\,s^{-1}$.

3. Results and discussion

As is evident from a typical cyclic voltammogram of the DMSO based electrolyte solution (see Fig. 1); there is no anodic faradaic process at potentials nega-tive to 1.0 V. Therefore all FTIR spectra were mea-sured at potentials positive to 1.0 V.

The infrared spectrum of DMSO was thoroughly studied in the early 1960s by King and Crawford [20] and by Carter *et al.* [21]. DMSO exhibits six infra-red active vibrations in the range between 4000 and $1000\,cm^{-1}$: $2973\,cm^{-1}$ ($\nu_{as.}$C–H), $2908\,cm^{-1}$ ($\nu_{sym.}$ C–H), 1440, 1410 and $1319\,cm^{-1}$ (δ CH_3) and $1050\,cm^{-1}$ (ν S=O)*. Dissolved electrolytes show absorption in the region around $1100\,cm^{-1}$. In the case of perchlorate solution the infrared spectrum contains a single peak of $\nu_{as.}$ Cl–O vibration of the ClO_4^- ion at $1100\,cm^{-1}$ [22]; in the case of tetrafluoro-borate solutions multiple absorption bands at 1100 and $1060\,cm^{-1}$ appear [23], but the latter peak is over-lapped by the strong absorption of ν S=O vibration of DMSO. Hexafluorophosphate anion absorbs out of the observable region [23].

3.1. Anodic oxidation

The results of spectroelectrochemical experiments are shown in Figs 2–6. Infrared spectra of anodic oxida-tion taken in solutions with different anions show no qualitative differences. Also the spectra measured on Pt and GC electrodes show negligible differences due to the varying size and reflectivity of the electrodes. Hence, the anodic decomposition of DMSO is not substantially affected by the electrode material and the supporting electrolyte. There are several positive peaks in the spectra at 3500, 2975, 2904, 1440, 1410, 1319 and 1050 cm^{-1}. All positive peaks, except the

* $\nu_{as.}$ asymmetric stretching vibration; $\nu_{sym.}$: symmetric stretching vibration; δ: bending vibration.
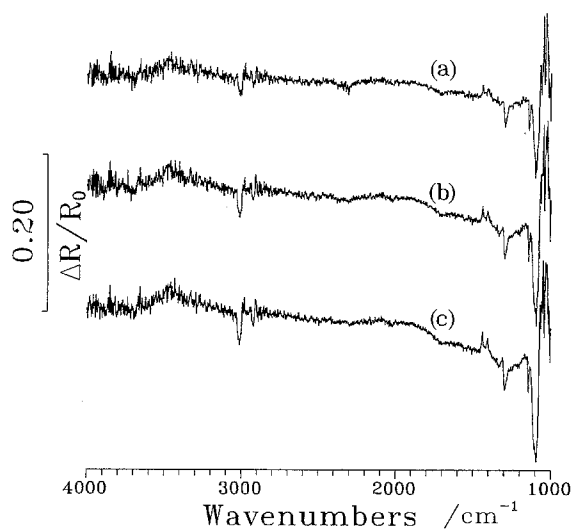
Fig. 2. SNIFTIR spectra of the Pt electrode in the 0.5 M $LiClO_4$/ DMSO solution. (0.04 M H_2O) after 5 min at: (a) 1.2, (b) 1.7 and (c) 2.0 V. Spectra were obtained by averaging of 70 spectral scans.

one at 3500 cm^{-1}, can be assigned to dimethyl sulfoxide. The peaks are upwards extending, that is, the DMSO is consumed at such conditions. The most intense peak at 1050 cm^{-1} corresponds to the S=O stretching vibration. Relatively high level of the noise around 1050 cm^{-1} is due to the low radiation flux close to the edge of the observable region. Positive bands of alkyl groups are less pronounced. As expected the S=O group is primarily affected by anodic oxidation. The positive peak at ca 3500 cm^{-1} can be attributed to the trace water depletion. We can also distinguish several downwards extending peaks in the spectra (peaks pointing to the more negative values of $\Delta R/R_0$ ratio). They appear at 3007, 2915, 1298 and 1140 cm^{-1}. This set of negative peaks is complemented by a single negative peak at 1104 cm^{-1}, observed in perchlorate containing solutions, or by a multiplet of negative peaks between 1100 and 1000 cm^{-1} in tetrafluoroborate solutions. All negative peaks in this spectral region can be assigned to the stretching vibration modes of perchlorate and tetrafluoroborate anions, respectively. The negative
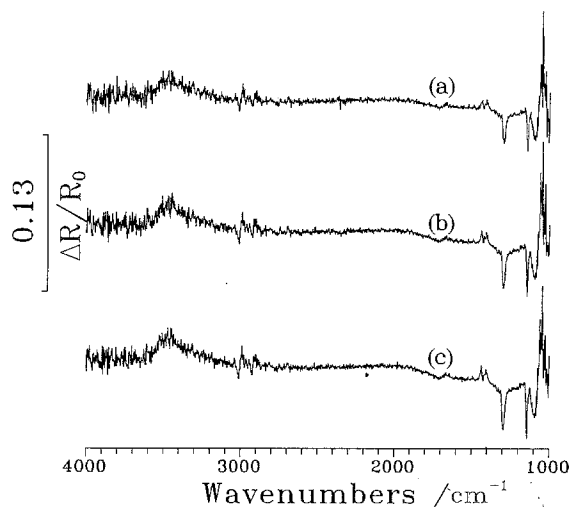

Fig. 3. SNIFTIR spectra of the Pt electrode in the 0.5 M $LiBF_4$/ DMSO solution (0.1 M H_2O) after 5 min at : (a) 1.2, (b) 1.7 and (c) 2.0 V. Spectra were obtained by averaging of 70 spectral scans.
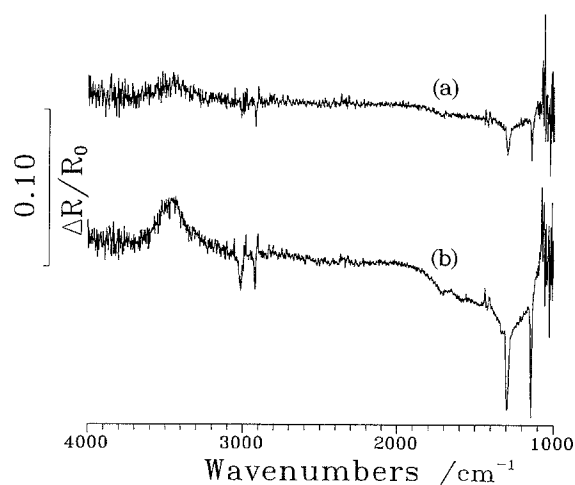

Fig. 4. SNIFTIR spectra of the Pt electrode in the 0.5 M $LiPF_6$/ DMSO solution. (0.06 M H_2O) after 5 min at: (a) 1.2, (b) 1.7 and (c) 2.0 V. Spectra were obtained by averaging of 70 spectral scans.

peaks at 1298 and 1140 cm^{-1} are of particular diagnostic significance. They may be assigned to the formation of SO_2 or SO_2 group in the system (the formation of dimethyl sulfone). The peak at 1298 cm^{-1} corresponds to the asymmetric stretching vibration of the SO_2 and the peak at 1140 cm^{-1} to the symmetric one (bending vibration of the SO_2 group appears out of the observable region). The frequencies of observed bands are slightly shifted from those of gaseous SO_2 [24] but the relative shift of ν_{as} and ν_{sym} agrees with theoretical predictions [25]. Also DMSO ex situ saturated with gaseous SO_2 exhibits a similar infrared spectrum. Since there is no other source of oxygen, the formation of SO_2 via reaction of trace water with DMSO might be expected and the oxidation process may be described as follows:

$$H_3C-S-CH_3 + H_2O \longrightarrow SO_2 + 2CH_4 \quad (1)$$
$$\overset{\|}{O}$$
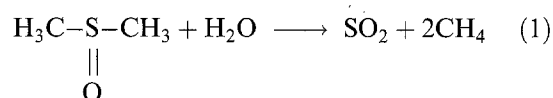
Reaction 1, however, does not explain the presence of strong negative absorption bands in the region 1100 and 1000 cm^{-1}, which correspond to an increase in anion concentration between electrode and optical window.

The presence of stretching vibration bands of the SO_2 group can be also explained in another way. The reaction of DMSO with water at the electrode may also lead to the formation of dimethyl sulfone and two protons. This hypothesis is supported by well pronounced negative peaks in the region between 3007 and 2900 cm^{-1} position of which is in accordance with alkyl vibrations of dimethyl sulfone. Nevertheless, no negative peaks appear in the region of bending vibrations between 1500–1300 cm^{-1}. The strong negative peaks around 1100 cm^{-1} may be assigned to ClO_4^- and BF_4^- anions [23]. The increase of the anion concentration in the layer between the optical window and positively polarized working electrode may generally be explained either by the double layer charging, or by the ingress of anions towards the working electrode, caused by a charge unbalance (e.g., due to the proton formation). The resulting signal in the case of DMSO based systems is a combination
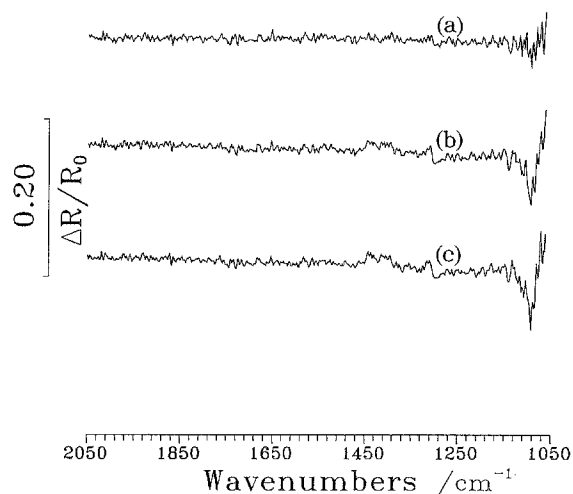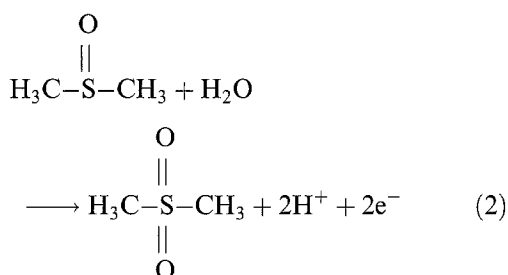
Fig. 5. SNIFTIR spectra of the illuminated *n*-TiO$_2$ electrode in the 0.5 M LiClO$_4$/DMSO solution (0.06 M H$_2$O) at 0.9 V (a) 70, (b) 160 and (c) 350 s after illumination. Spectra were obtained by averaging of 70 spectral scans.

Fig. 6. SNIFTIR spectra of the illuminated *n*-TiO$_2$ electrode in the 0.5 M LiPF$_6$/DMSO solution (0.06 M H$_2$O) containing 0.5 M Bu$_4$NI at 0.9 V: (a) 70, (b) 160 and (c) 350 s after illumination. Spectra were obtained by averaging of 70 spectral scans.

of both contributions, the charge unbalance is, however, the prevailing process. The proposed process may be described as follows:

$$H_3C-\overset{\overset{\displaystyle O}{\|}}{S}-CH_3 + H_2O$$

$$\longrightarrow H_3C-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-CH_3 + 2H^+ + 2e^- \qquad (2)$$

The correct assignment of the main decomposition product of dimethyl sulfoxide based solutions solely on FTIR data is not possible. Therefore an independent method (GC–MS) was used (*vide infra*).

3.2. *Photoanodic oxidation on TiO$_2$*

3.2.1. *Absence of nucleophilic agent.*
In the absence of a nucleophilic agent, the FTIR spectra on the illuminated TiO$_2$ (anatase) electrode resemble those on Pt electrodes (see Fig. 5). The decomposition process is presumably identical as in the case of anodic decomposition on Pt and GC in the dark. The poor signal to noise ratio is due to the lower reflectivity of TiO$_2$ electrodes.

3.2.2. *Presence of nucleophilic agent.*
The spectra of DMSO/KPF$_6$ system containing 0.5 M of tetrabutylammonium iodide (Bu$_4$NI) are shown in Fig. 6. FTR spectra of photoelectrochemical degradation in the presence of I$^-$ differ substantially from those mentioned in Section 3.2.1. The prevailing redox process, proceeding in the system at these conditions, is the oxidation of I$^-$ to I$_3^-$. The charge unbalance caused by consumption of anions at the electrode triggers the transport of ions to and from the electrode (cations move from and anions move to the electrode) to compensate the charge unbalance. These processes are represented in FTIR
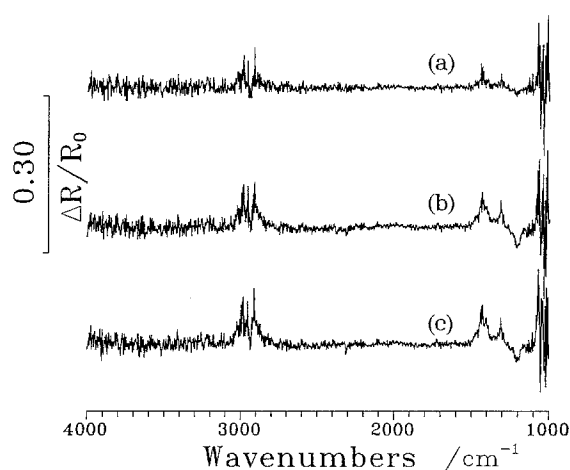
spectra by a strong positive absorption band in the C–H stretching vibration region around 3000 cm^{-1}. This absorption corresponds to the stretching vibrations of Bu$_4$N$^+$ and indicates egress of cations from the layer between the electrode and the optical window. This positive absorption band is composed of several peaks, which cannot be precisely distinguished due to the poor electrode reflectivity. Complementary process to the cation egress is a transport of anions into the layer between the optical window and the working electrode. A direct evidence of this process, based on infrared spectroscopy is, however, inaccessible, because all anions present in the system (PF$_6^-$, I$^-$ and I$_3^-$) are either spectroscopically inactive (I$^-$) or absorb below 1000 cm^{-1} (PF$_6^-$, I$_3^-$). Three positive peaks also appear in the region of bending vibration of the alkyl group. These peaks are of the same position and shape as that of pure DMSO (1440, 1410 and 1319 cm^{-1}). The presence of these peaks indicates that the DMSO molecule may be involved in the photoanodic process. This seems to be supported by the presence of a negative peak at 1210 cm^{-1}. This band may be assigned, with respect to the composition of the system, to the S=O stretching vibration of an alkylsulfinylhalogenide [21], probably of methylsulfinyliodide. It handicaps DMSO as a solvent for photovoltaic cells with TiO$_2$ (anatase) photoanodes. Similar behaviour, that is, reaction of one of the charge mediator forms with intermediates of photoanodic solvent decomposition forming electrochemically inactive compound, was observed by photoanodic oxidation of propylene carbonate based electrolyte solution [14].

3.3. *GC–MS measurements*

To distinguish between two possible breakdown pathways in DMSO based systems, potentiostatic electrolysis followed by *ex situ* GC–MS analysis was used. LiBF$_4$/DMSO solution (15 ml, 0.5 M) was potentiostatically electrolysed in a two-compartment cell

using a platinum anode at potential 1.4 V vs SCE for several days. The anolyte was subsequently analysed by GC–MS. It was free of sulfur dioxide, as well as of methane or any other alkane. This fact excludes the breakdown of DMSO according to Equation 1 and supports the formation of dimethylsulfone.

4. Conclusion

The dimethyl sulfoxide based solutions are unstable at potentials positive to 1.0 V. The DMSO breakdown is initiated by trace water oxidation and dimethyl sulfone and protons are formed. The course of decomposition does not depend on the supporting electrolyte nor on the electrode material. The photoanodic oxidation of dimethyl sulfoxide based solutions proceeds by the same mechanism as the anodic oxidation. The addition of a nucleophilic agent (Bu_4NI) changes the path of photoanodic reaction. The main process is the oxidation of iodides to triiodides, but small amounts of methylsulfinyliodide are probably formed. Such behaviour resembles that of propylene carbonate based solutions [14] and shows the importance of appropriate solvent as well as the charge mediator selection for practical solar cells design.

Acknowledgements

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