Proceedings of the 3rd World Congress on Momentum, Heat and Mass Transfer (MHMT'18)
Budapest, Hungary – April 12 - 14, 2018
Paper No. ICHTD 103
DOI: 10.11159/ichtd18.103

Electrochromics for Thermal Control on Spacecraft

Oliver Kluge[1], Barbara Abendroth[2], Thomas Köhler[2], Martin Altenburg[3], Lars Borchardt[4], Elisabeth Abbe[1], Tilman Schüler[1], Alexander Zwiebler[1], Martin Tajmar[1], Tino Schmiel[1]
[1]Institute of Aerospace Engineering, Technische Universität Dresden
01062, Dresden, Germany
oliver.kluge@tu-dresden.de
[2]Institue of Experimental Physics, TUBA Freiberg
09599, Freiberg, Germany
[3]Airbus Defence & Space GmbH
88090, Immenstaad, Germany
[4]Institute of Inorganic Chemistry
01062, Dresden, Germany

Abstract - Orbital spacecrafts face the problem of high thermal gradients or different thermal loads mediated by differential illumination from the sun. As spacecrafts are limited in weight there is a growing interest in heat transfer solutions, which are lightweight and economical. Variable electrochromic radiation heat transfer is a promising approach as it offers a better mass budget by saving heater power in the coldest boundary conditions. The focus of the present work is on the engineering and the material science of such electrochromic radiators, which are based on electrochemical cells and the intercalation of Li^+-Ions into transition-metal-oxides. Samples out of soda lime glass, Kapton and high thermal conductive pyrolytic graphite foil, with different absorption modulation, are prepared by the use of reactive magnetron sputtering and electrochemical intercalation. The purpose of this work is represented by maximizing the $\Delta\alpha$ and $\Delta\varepsilon$, feasibility of oppositional α/ε modulation, different substrate testing and relate the results with preliminary on-orbit simulations. Several concepts of electrochromic radiators are investigated in the last years. They are made out of full solid state materials or implemented with electrolyte-polymers and a $\Delta\varepsilon$ up to 0.5 and still high absorptivity. We found a modulation range of -0.14 up to 0.23 for the infrared emissivity and 0.43 up to 0.58 for transmittance in the spectral range of 300 to 1000 nm in the case of single layers. Aluminized Kapton shows twice as high absorption modifications as aluminized graphite foil, which is caused by the intercalation of Li^+ in the graphite-structure instead of tungsten oxide. The modulation is not yet sufficient in range and it's oppositional α/ε. The pyrolytic graphite foils are not suitable for direct deposition of the electrochromic stack and should be used for thermal distribution only. According to the experimental data, a simple stack with a $\Delta\varepsilon$ in the range of 0.21 to 0.29 seems to be realizable.

Keywords**:** Electrochromic, Radiator, Spacecraft, Heat, Variable, Optical, Modulation.

1. Introduction

The design of thermal control systems (TCS) on spacecrafts is driven by thermal extrema in the space environment. It ensures the stability of the payload function on the specified mission. The coldest and hottest boundary condition are represented by cold- and hot-case, respectively. Basically, the surface of the radiator is calculated by the amount of heat that requires to be dissipated to deep space. In contrast, heating technologies such as heaters, heat-pipes or heat-switches are deployed to ensure the survival of the payload in the cold-case. To overcome the usual higher power/mass budge, a radiator with variable optical properties is chosen. By careful adjustment of both emissivity (ε) and solar absorptivity (α), an electrochromic radiator can repeal such a limitation. Fig. 1 show the exemplary result of thermal simulations for a payload on the earth observation satellite Sentinel 2 (Thermal Model) and its comparison between the state-of-the-art radiator (SAR) and a theoretical electrochromic-variable radiator (ECR) with the software ESATAN-TMS [1]. One important characteristic of the Sentinel 2 TCS is the integration of payloads outside the main structure e.g. prime and redundant batteries. This payload has their own radiators and is located on the nadir panel with radiative couplings to Earth-IR, Albedo und partly direct solar flux. Temperatures below the lower threshold results in an activation of the heater and they keep being active until temperature reaches the upper threshold. These simulations show, that power savings (e.g. for payload heating) >95% are possible for Δε>0.4 [1].

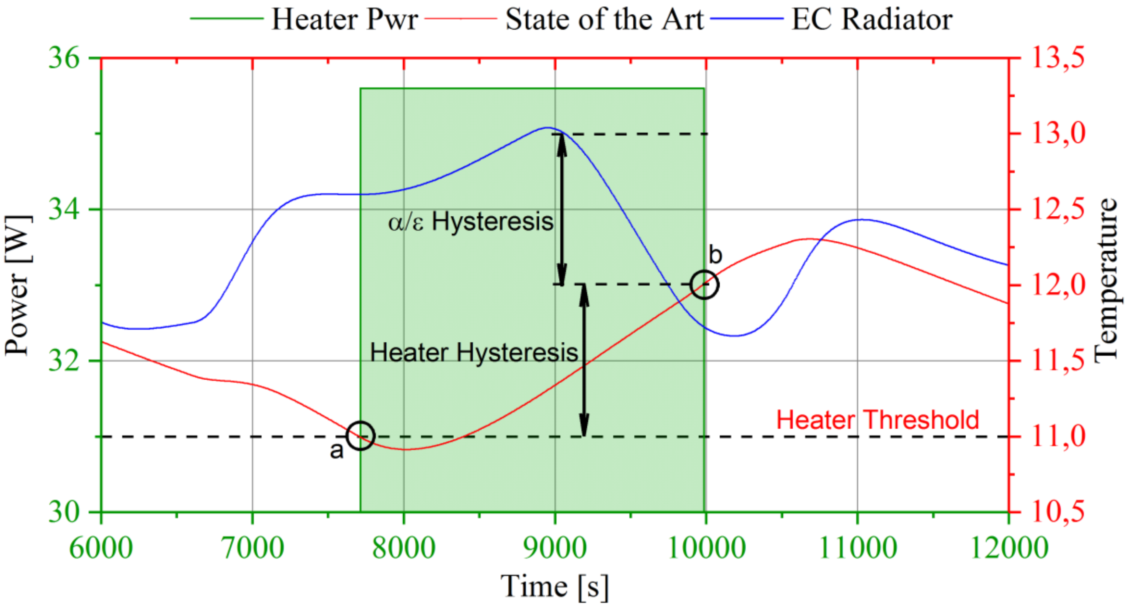

Fig. 1: Thermal simulations on Sentinel 2: ECR hysteresis between 12 and 13 °C, SAR heater hysteresis between 11 and 12 °C. Heater activation (during a to b) is prevented by variable optical properties for saving electrical energy [1]. Blue: Temperature with ECR; Red: Temperature with SAR; Green: Heater power with SAR.

ECRs for a variable rejection of dissipated heat are reviewed in earlier literature [2] [3] and [4] and devices with a Δε up to 0.5 have been developed and successfully tested previously [5] [6]. The samples manufactured by Chandrasekhar [5] can adjust the emissivity and absorptivity - but not vice versa. So both are modulated at the same time and a relatively high absorptivity follows to a high emissivity. By optimising the maximum cooling capacity towards maximum emissivity and minimum absorptivity within the hot-case, the best benefit in mass-budget will be reached. Higher "solar" absorptivity remove this effort during direct or indirect (Albedo) solar radiation. Indeed, Eclipse Energy Systems make use of techniques like cold-mirrors to avoid such limitations [6]. An ECR with variable emissivity and absorptivity is currently developed at TU-Dresden. It promised advantages including scalable production, less thermal gradients or thermal noise and a simplification of design justification.

2. Description

The electrochromic effect in transition-metal oxides was described in 1969 by S.K. Deb [7]. Electrochromics can adjust the density of absorbed visible light and are applied for architecture and glasses. The electrochromic effect causes a modification in the absorption of electromagnetic waves due to reducing the tungsten content and accordingly the shift of the Fermi level into the next higher band by the intercalation of alkali metals or hydrogen in WO_{3-y} [2] [3]. The extreme states of the optical modulation are called "bleached" for low absorption and "colored" for high absorption. The idea of a variable emissivity can be implemented as a variable reflectance according to ε' = α' = 1 – R [8]. The hemispheric total emissivity is defined by:

$$\varepsilon(T_A) = \frac{\int_0^\infty \varepsilon_\lambda(\lambda, T_\mathrm{A}) e_{\lambda\mathrm{b}}(\lambda, T_\mathrm{A}) \mathrm{d}\lambda}{\sigma T_\mathrm{A}^4} \tag{1}$$

where ε_λ is the hemispherical spectral emissivity, $e_{\lambda b}$ the radiative emissive power (Planck's law), T_A the surface temperature, λ the wavelength and σ the Stefan-Boltzmann constant [8].

The total power of radiated heat transferred to the space environment ($T_\mathrm{space} = 3\,\mathrm{K}$) is defined by [9]:

$$\dot{Q}(T_A) = \varepsilon\sigma A(T_\mathrm{A}^4 - T_\mathrm{space}^4) \tag{2}$$

For the measurement of the hemispheric total emissivity a diffuse reflectance accessory with integrating sphere is needed, however, for the evaluation and measurement purpose of the different absorption modifications in tungsten oxide, bidirectional spectral reflectivity or transmission is sufficient. Fig. 2 shows a qualitative sketch of such a radiator concept and its optical measurement. The solar absorptivity (α) and infrared emissivity (ε) is usually measured in the spectral range from 0.25 to 2.5 µm and 3 to 2 µm, respectively, according to the European Cooperation of Space Standardization (ECSS) [10]. Since the absorptivity-difference (Δα) is evaluated on different substrates, the measurement has been done in the spectral range from 0.3 to 1.0 µm for absorptivity and the full infrared (3 to 2 µm).

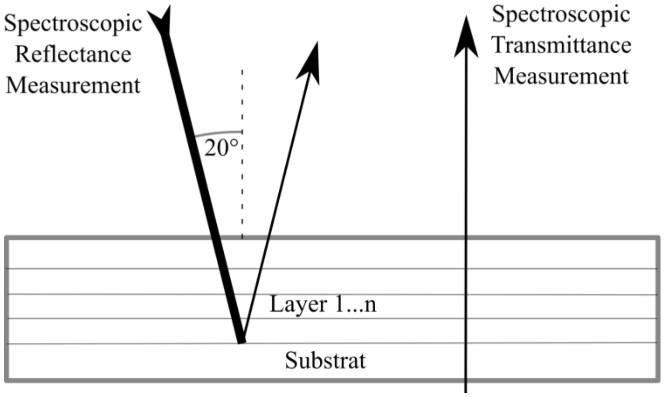

Fig. 2: Schematic electrochromic radiator and measurement concept. Variable emissivity can be implemented as a variable reflectance on a highly reflective substrate according to ε' = α' = 1 – R [8].

3. Fabrication

There are different behaviours of intercalated WO_{3-y} according to the parameters of the deposition process and method itself. Literature [11], [12] reports that an increasing amount of intercalated lithium leads to an increased absorption in the visible spectrum, whereas changes in the infrared spectrum depends on the crystal structure. Nanocrystalline and polycrystalline WO_{3-y} show opposing absorption properties which is associated with intercalated Li^+. The heat-treatment temperature and porousness also affects the spectral characteristics of tungsten oxide [13] [14]. The aim of our work is improving electrochromic radiator technology in terms of optimising the absorption characteristics of Li^+ intercalated tungsten oxide on different substrates.

Fig. 3 shows the steps of preparation, intercalation and measurement of half electrochromic cells.

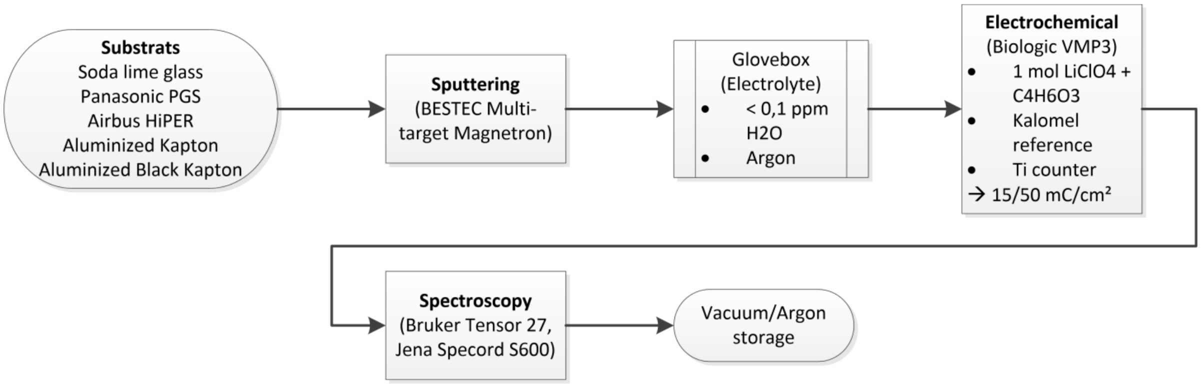

Fig. 3: Procedure for sputtering, electrochemical intercalation and spectroscopy.

Tungsten oxide is deposited by reactive magnetron sputtering with different parameters to reach the Nano-/polycrystalline condition. Technically, the intercalation of Li^+ into tungsten oxide has been achieved on an area of 2 cm² masked by polyimide foil, charged in 1 mol lithium perchlorate and propylencarbonat electrolyte using a Biologic VMP3 potentiostat and finally cleaned with ethanol. For spectroscopy a Jena Analytic Specord S600 (UV-Vis) and Bruker Tensor 27 (FTIR) is applied. Tab. 1 shows the sputtering parameters, which are used for different substrates.

These are soda lime glass slides, pyrolytic graphite foil (Airbus Defence & Space GmbH [15] and Panasonic Europe [16]), aluminized Kapton (polyimide, Sheldahl) and aluminized Kapton B. Pyrolytic graphite foil (Panasonic Europe) can achieve values for thermal conductivity up to 1950 W/(m*K) [16], that allows the implementation of radiator foils without complete contacting to the structure and consequently results in mass savings. Kapton or Kapton Black (B) can be applied as an alternative or in combination with graphite foil instead of state-of-the-art massive radiator structures like second surface mirrors (SSM), that are made of aluminized silica glass. The graphite and Kapton B foils are not smooth, so the bidirectional spectral reflectivity measurement does not show absorption near to hemispheric values, However, the measurements related to the $\Delta\alpha$ are comparable. A part of the solar spectrum is aimed to be characterised for the foils thus amorph tungsten oxide sputtered at room temperature (RT) was used. Thicknesses of the deposited layers are routinely measured by ellipsometrie (Woollam M-200) on silicon wafer substrate. The samples are measured on different points and averaged for calculation and plotting.

Table 1: Parameters for reactive magnetron sputtering: Transmission on glossy surfaces with Indium-Tin-Oxide (ITO): 1,2,3; IR-reflectance: 2,3; solar-reflectance: 4,5,6,7.

(Sample) Substrat	(1) Glass + ITO	(2) Glass + ITO	(3) Glass + ITO	(4) Panasonic PGS + Al	(5) AIRBUS HiPER + Al	(6) Kapton + Al	(7) Black Kapton + Al
Ar [sccm]	23.5	23.5	23.5	23.5	23.5	23.5	23.5
O2 [sccm]	5	5	8	6	6	6	6
Power [W]	150	150	150	150	150	150	150
Pressure [mbar]	6,2e-3	6,1e-1	5,8e-3	6,4e-3	6,3e-3	6,3e-3	6,2e-3
Thickness ITO [nm]	291	291	275	-	-	-	-
Thickness WO_{3-y} [nm]	300	300	157	271	271	271	271
Temperature [°C]	RT	RT + heat-treatment at 450 °C	400 °C substrate heating	RT	RT	RT	RT
Intercalation [mC/cm²]	50	15	50	50	50	50	50

4. Results and Discussion

The expected results are the opposing absorption in the solar and infrared spectral range, associated with the intercalated Li^+ on deposited glass and significant variances on the deposited foils. We show the different behaviour of the tungsten oxide phases. According to Larsson [11] [12] and Chang-Yeul [13], the transmittance and reflectance shows the behaviour of amorph, nanocrystalline and polycrystalline tungsten oxide in Figure 4 and 5 respectively. This can be observed by the varying modification of the absorption behaviour during Li^+ intercalation. Sample 3 with direct substrate heating in the sputtering process has an increasing reflectance in the intercalated state, which was observed in the polycrystalline phase. Sample 2 was sputtered at room temperature with an amorphous state and heat-treated at 450 °C for 2 h non-evacuated to a potentially nanocrystalline phase [11]. The a-WO_{3-y} sample 1 shows an upper regulation of the solar absorptivity and infrared emissivity, see figure 4 and 5. Furthermore the glass samples (1,2,3) show a strong lattice absorption of the metal oxides (c-WO_3, a-WO_3) [4] at ~10 µm.

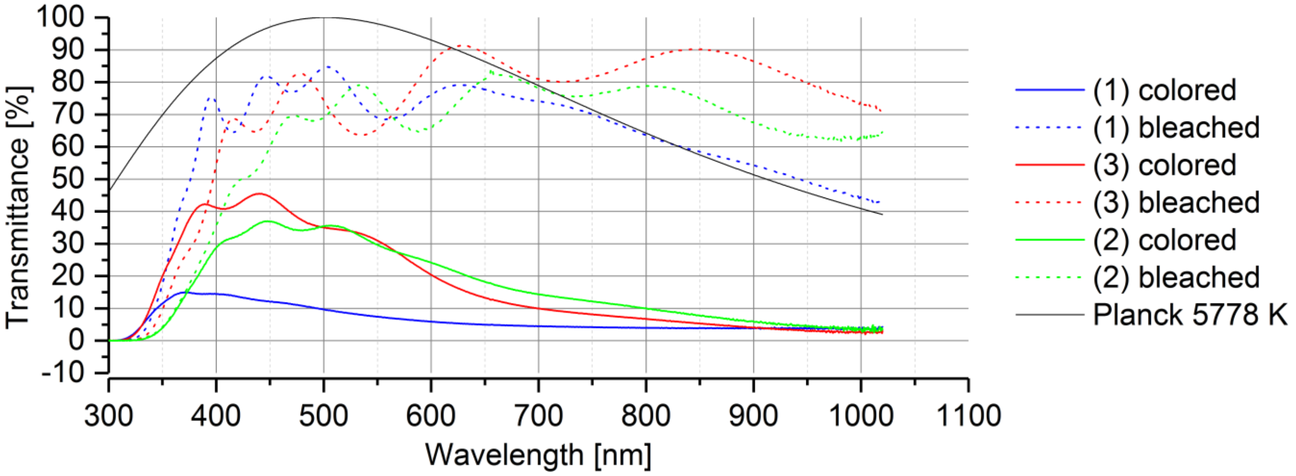

Fig. 4: UV/Vis spectra of glass + ITO + WO_{3-y}; transmittance measurement; 1: amorphous, 2: heat-treated 450 °C, 3: direct substrate heating 400 °C; Planck black body at 5778 K.

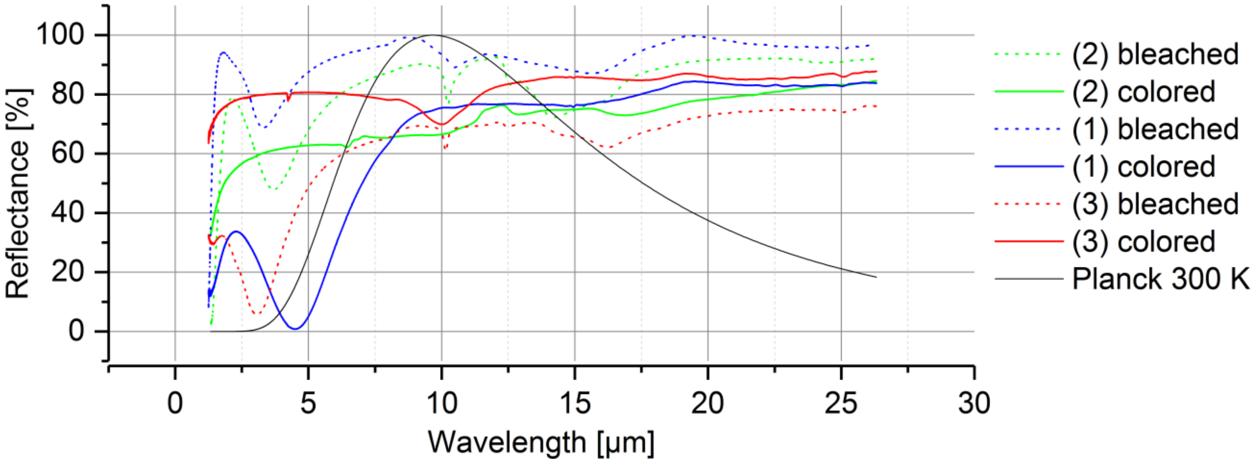

Fig. 5: Infrared spectra of glass + ITO + WO_{3-y}; reflectance measurement; 1: amorphous, 2: heat-treated 450 °C, 3: direct substrate heating 400 °C; Planck black body at 300 K.

According to lightweight radiator concepts, the samples 4 - 7 are sputtered on foils coming from experimental aluminized pyrolytic graphite and ex-factory aluminized Kapton (polyimide). It can be observed in figure 6 and 7, that the modulation range ($\Delta\alpha$) of matt aluminized Kapton B surface is nearby the glossy surface of the aluminized Kapton. According to Guofa [14] and Stiebich [17], WO_{3-y} prepared by sputtering on rough surfaces should show a larger modulation between the bleached and colored state caused by higher WO_{3-y} surfaces. The ratio of $\alpha_{bleached}/\alpha_{colored}$ of the aluminized graphite sheets is lower than aluminzed Kapton which was not expected. A Li^+ intercalation into pure graphite foil confirmed the assumption that Li^+ was partly intercalated into the graphite structure. This is similar to the emplacement of Li-Ions in the electrodes Li-Ion batteries. Due to interference effects for λ/4-layer, a wavelength-dependence is visible, especially on the substrate with ITO and WO_{3-y}.

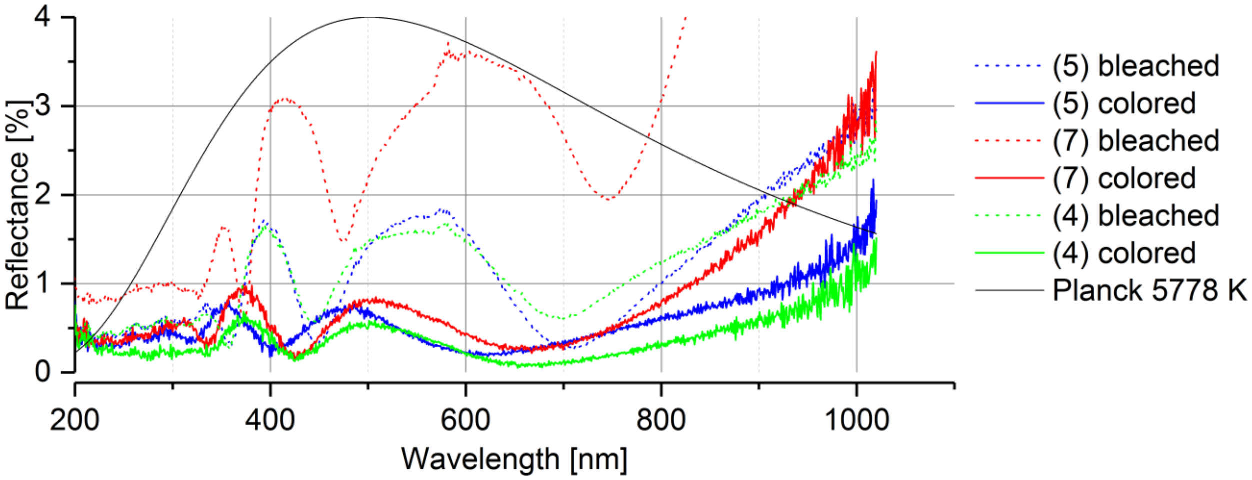

Fig. 6: UV/Vis spectra of graphite-foil/Kapton-Black + WO_{3-y}; reflectance measurement; 4: Panasonic PGS + amorphous, 5: AIRBUS HiPER + amorphous, 7: Kapton Black + amorphous; Planck black body at 5778 K.

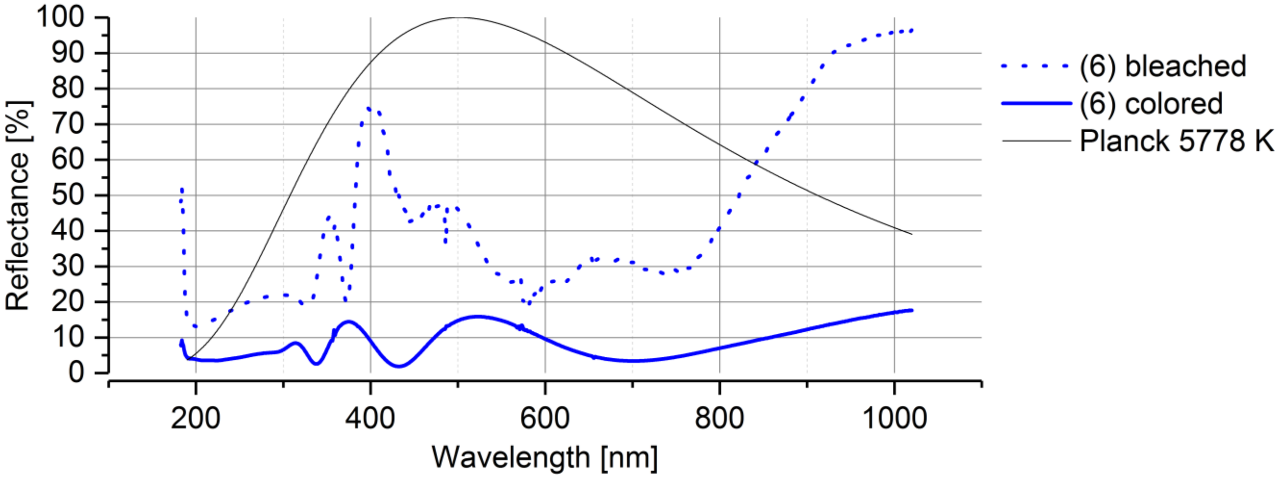

Fig. 7: UV/Vis spectra of Kapton + WO_{3-y}; reflectance measurement; 4: Kapton + amorphous; Planck black body at 5778 K.

Table 2: Spectroscopic (FTIR, UV-Vis) results. Bold values represent the maximum performance. Δα: with transmittance (T) or reflectance (R); Δε: with reflectance in the infrared spectral range according to ECSS-Q-ST-70-09C.

Substrat	(1) Glass + ITO	(2) Glass + ITO	(3) Glass + ITO	(4) Panasonic PGS + Al	(5) AIRBUS HiPER + Al	(6) Kapton + Al	(7) Black Kapton + Al
$\Delta\alpha$'(300-1000)nm	0.58 (T)	0.43 (T)	0.51 (T)	0.78e-2 (R)	0.63e-2 (R)	**0.33** (R)	0.028(R)
$\alpha_{\text{bleached}}/\alpha_{\text{colored}}$	**9.1**	3.3	3.5	3.2	2.2	4.7	**4.8**
$\Delta\varepsilon$ (3-21)µm	**0.23**	0.14	-0.14	-	-	-	-

The accuracy of the results was not determined by the measurement error itself. Inhomogeneity's caused by sputtering, intercalation or the waviness of the foil substrates are significantly higher and creates a coefficient of variation up to 0.3 for the Δα of Kapton + Al + WO_{3-y}.

5. Conclusion

The present work demonstrates the absorption modifications of tungsten oxide in bleached and Li(+) intercalated state of amorph, poly- and nanocrystalline phase suitable for lightweight electrochromic radiators on spacecraft. The modulation range of -0.14 up to 0.23 for the infrared emissivity and 0.43 up to 0.58 for the transmission in the spectral range of 300-1000 nm are not yet sufficient for the application of electrochromic radiators, which needs a $\Delta\varepsilon > 0.4$ [1]. Based on the results of this work an electrochromic radiator with tungsten oxide in the nano- and polycrystalline phase needs more investigation. This combination summates both infrared modulations to a higher $\Delta\varepsilon$ caused by the oppositional behaviour in the Li^+ intercalation process. According to the experimental data, a simple stack with a $\Delta\varepsilon$ in the range of 0.21 to 0.29 and the restriction of a still high solar absorption seems to be realizable. Other Substrate or heat-treatment temperatures will be tested as soon as possible to realize a permanently high transmission of electromagnetic waves in the infrared at high solar absorption (α). In addition work on new concepts for an oppositional modulation in the solar and infrared spectrum is ongoing. The soda lime glass does not show any kind of modulation in the UV due to the absorption of electromagnetic waves related to the material properties. By comparing sputtered WO_{3-y} on different foils, differences in the absorption can be observed. Sputtering and electrochemical intercalation on aluminized pyrolytic graphite foil shows a significant lower modulation in comparison to glossy aluminized Kapton or matt Kapton B. The modulation of tungsten oxide on aluminized Kapton B shows expected values that are twice as high compared to the aluminized graphite foils. Those differences in the absorption of aluminized Kapton/graphite were caused by intercalated Li^+ in the graphite-structure instead of the tungsten oxide, similar to the emplacement of Li-Ions in the electrodes Li-Ion batteries.

Acknowledgements

The authors would like to thank the TU Bergakademie Freiberg and the chair for inorganic chemistry of the Technische Universität Dresden for their support. Special thanks are going to Günter Gärtner, Desirée Leistenschneider, Claudia Schenk and Robert Toschka for their help in spectroscopy, chemistry and transcription. Also thanks going to Airbus Defence & Space GmbH and Panasonic Europe for the several substrates. This work was partly funded by Deutsches Zentrum für Luft- und Raumfahrt (DLR) on behalf of Bundesministerium für Wirtschaft und Energie (BMWi, FKZ50RM1520)

References

[1] O. Kluge, A. Zwiebler, T. Schmiel, M. Altenburg und M. Tajmar, *Thermal Analysis of Electrochromic Radiators on Sentinel 2,* Bd. 31st European Space Thermal Analysis Workshop, Noordwijik: ESTEC, 2017.

[2] L. Berggren, "Optical Absorption and Electrical Conductivity in Lithium Intercalated Amorphous Tungsten Oxide Films," Ph.D. disseration Hrsg., A. U. Upsaliensis, Hrsg., Uppsala, Uppsala län: Uppsala University, 2004.

[3] A.-L. Larsson, "All-Thin-Film Electrochromic Devices for Optical and Thermal Modulation," Ph.D. disseration Hrsg., A. U. Upsaliensis, Hrsg., Uppsala, Uppsala län: Uppsala University, 2004.

[4] E. B. Franke, C. L. Trimple, J. S. Hale, M. Schubert und J. A. Woollam, "Infrared switching electrochromic devices based on tungsten oxide," *Journal of applied physics,* vol. 88, no. 10, 2000.

[5] P. Chandrasekhar, B. J. Zay, D. Lawrence, E. Caldwell, R. Sheth, R. Stephan und J. Cornwell, "Variable-Emittance Infrared Electrochromic Skins Combining Unique Conducting Polymers, Ionic Liquid Electrolytes, Microporous Polymer Membranes, and Semiconductor/Polymer Coatings, for Spacecraft Thermal Control," *Journal of Applied Polymer Science,* p. 18, 2014.

[6] E. F. Agasid und K. C. Shannon III, "Variable Emittance Electrochromic Thermal Control for Small Satellites," *Presentation.*

[7] S. K. Deb, "A Novel Electrophotographic System," *Applied Optics*, pp. 192-195, 1969.

[8] R. Siegel und J. R. Howell, Thermal Radiation Heat Transfer, T. &. Francis, Hrsg., Washington, DC: Hemisphere Publishing Corporation, 1992.

[9] D. G. Gilmore, *Satellite thermal control handbook*, vol. 1. El Segundo, Calif.: The Aerospace Corporation, 2001.

[10] ESA-ESTEC, ECSS-Q-ST-70-09C, "Measurements of thermo-optical properties of thermal control materials", Noordwjik: ESA-ESTEC, 2008.

[11] A.-L. Larsson, J. Solis und G. A. Niklasson, "Infrared absorption in Li-intercalated tungsten oxide," *Solar Energy Materials and Solar Cells,* pp. 1248-1252, 15 August 2007.

[12] A.-L. Larsson, B. E. Sernelius und G. A. Niklasson, "Optical absorption of Li-intercalated polychristalline tungsten

oxide films: comparison to large polaron theory," *Solid State Ionics*, no. 165, pp. 35-41, 2003.

[13] K. Chang-Yeoul und S. Park, "Electrochromic Properties of WO3 Thin Films with various Heat-Treatment Temperature," *Asien Journal of Chemistry*, no. 25, pp. 5874-5878, 2013.

[14] G. Cai, M. Cui, V. Kumar, P. Darmawan, J. Wang, X. Wang, A. L.-S. Eh, K. Qian und P. S. Lee, "Ultra-large optical modulation of electrochromic porous WO3 film and the local monitoring of redox activity," *Royal Society of Chemistry*, no. 7, pp. 1373-1382, 2016.

[15] B. Benthem und F. Mena, "Innovative new High Performance Radiators: Developing heat rejection systems with flexible film technology," *International Conference on Environmental Systems*, p. 20, 2015.

[16] Panasonic, "Panasonic Industrial," [Online]. Available: https://industrial.panasonic.com/cdbs/www-data/pdf/AYA0000/AYA0000C27.pdf. [Accessed 11 October 2017].

[17] J. Stiebich, "Elektrochrome Beschichtungen: Herstellung und Analyse von elektrochromen Metalloxiden," Ph.D. Dissertation Hrsg., 1. P. Institut, Hrsg., Gießen, Hessen: Justus-Liebig-Universität Gießen, 2009.