Molecular Level Description of the Ni-based, Ligand-Exchange Thermochromic Process

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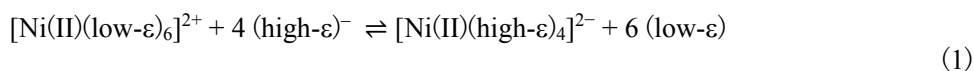
Thermochromic interlayer (marketed as Suntuitive® films) darkens reversibly when heated by direct sunlight. The underlying chemical phenomenon is the temperature dependent, dynamic ligand-exchange process that facilitates changes in the coordination environment of the chromophore Ni complexes. X-ray absorption spectroscopic measurements were carried out at various temperatures for commercials films and model solutions to follow the electronic (from XANES) and geometric (from EXAFS) structural changes. We identified pre-edge and rising-edge features for model complexes that can be used to deconvolute the spectral changes of thermochromic films. We observe that the model solutions mimic only in part the behaviour of commercial samples as a function of temperature.

Keywords :   thermochromism, nickel-halide complexes, ligand-exchange equilibrium, pre-edge features

Background and Objective :
Windows are one of the most critical components of buildings with respect of energy conservation and functionality [1]. Unfortunately, these two aspects work against each other, where shades and tinting may reduce the direct heat load from the sun, but block the natural light and visibility. The latter has been related to performance loss and health issues. Many solutions have appeared recently on the market for optimizing window performance and energy consumption of heating or air-conditioning. The two leading solutions are offered by electrochromic and thermochromic technologies. The former is only solving part of the problem, since control units and electricity are needed for darkening the windows to cut down the heat load from direct sunlight. On the contrary, thermochromic process allows for the darkening without any control mechanism. A chemical change resulting in darkening in a thermochromic film laminated between two sheets of glass is triggered by heating up of the window in direct sunlight and clearing up to allow daylight into the room when then there is no direct sunlight on the window pane.

The ligand-exchange thermochromic change in the "Suntuitive®" interlayer developed and manufactured by Pleotint LLC [2] is based on a dynamic equilibrium between two coordination chemistry environments with different types and number of ligands. These define the positive entropy and the positive enthalpy changes as shown in Eq.(1), which is an example of an equation for the thermochromic process.

$$[Ni(II)(low\text{-}\varepsilon)_6]^{2+} + 4\ (high\text{-}\varepsilon)^- \rightleftharpoons [Ni(II)(high\text{-}\varepsilon)_4]^{2-} + 6\ (low\text{-}\varepsilon)$$

$$\Delta G^{rxn}(T) = \Delta H^0 - T\Delta S^0 + RT \ln Q$$

(1)

The standard enthalpy change (ΔH^0) is determined by the number and nature of metal-ligand interactions and to a significant degree the interaction of the non-coordinated ions or ligands within the polymer matrix. The entropy change (ΔS^0) is associated with the reorganization of the inner sphere coordination environment and the polymer environment as the ligands move in and out of the bulk and into the Ni(II) coordination sphere. The reaction quotient (Q) has also a great importance, since the concentrations of the low- and high-ε ligands need to be tuned to provide the crossover temperature at around 50 °C. The nature of the counter ions is crucial, since inorganic cations tend to supress the thermochromic process in the ambient temperature range over organic cations, such as tetraalkyl ammonium cations as they have lower tendency to ion pair with halide ligands as compared to inorganic cations.

The "low temperature", left-hand side of this equilibrium contains a hexacoordinate Ni(II) complex coordinated with presumably ROH groups from the polymer matrix (polyvinyl butyral resin) and the added low-ε ligand (multi-dentate alcohols), where "ε" refers to the molar extinction coefficient of the resulting coordination compound. The "high temperature", right-hand side of the equilibrium contains the coloured compound with four-coordinate Ni(II) environment and due to a combination of halide ions and

N-heterocyclic high-ε ligands. Changes in the coordination environment due to ligands coming and going from the inner sphere environment can be directly probed by X-ray absorption spectroscopy.

The understanding of the molecular processes during a temperature dependent change can provide the experimental handle to probe, optimize, and develop thermochromic materials. Currently, this development is done primarily with a trial-and-error approach capitalizing on a large library of thermochromic systems that has already been established at Pleotint LLC. During the first series of measurements, we focused on commercial films prepared under various conditions and exposed to Xe-arc lamp in a Weather-ometer® that provide accelerated aging of the films. Additional set of samples either recovered from installations, or saved from the production line are available that are associated with some type of issue in window performance. The XAS measurements combined with computational modelling [3] provide a pathway to understand the source of performance issues. Furthermore, the results from the XAS measurements contribute to further optimizing the thermochromic materials by increasing thermochromic film performance and durability.

Experiments :

The sample measurements were carried out in a custom build chamber by Pleotint LLC, as shown in Figure 1. The ionization chambers were protected with a 5 mil or 0.13 mm thin Kapton film. The temperature controller was calibrated before the measurements. The temperature was scanned from room temperature to 125 ºC in 25 ºC steps. It is worth noting that the current setup is ideal for converting the sample stage to be compatible with fluorescence detection. Given the concentration of the elements of interests, the use of passivated implanted planar silicon (PIPS) detector (Canberra) would be sufficient since that does not require gas purge such as the Lytle detector and is non-sensitive to temperature, such as the multi-element detector.
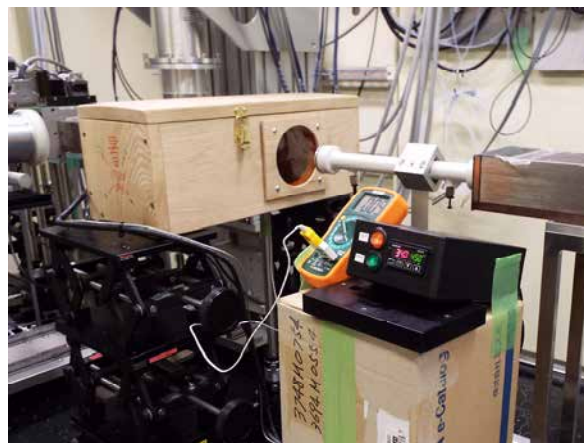

Fig.1. Experimental sample stage for transmission measurements with the temperature control unit (black) and multi-meter (orange) attached to a thermocouple placed next to the sample.

X-ray absorption fine-structure (XAFS) measurements were carried out at BL14B2 in the hard X-ray energy region, at the Ni K- (8 keV), Br K- (13.5 keV), and I (33 keV) K-edges. The use of the unique auto-sampler setup allowed the rapid and efficient establishment of the reference spectra for compositionally and structurally well-defined hexa- and tetra-coordinated Ni(II) complexes. We have used the standard transmission setup for bulk XANES and EXAFS measurements in rapid scan operation mode. Fluorescence measurements would allow for detecting changes of complexes in smaller concentrations.

Four groups of samples were analysed. Group 1 contained the structurally well-defined Ni(II) complexes that correspond to either low-temperature or high temperature speciation. These include $Ni(ClO_4)_2 \cdot 6H_2O$, $NiCO_3$, NiF_2, $NiCl_2$, $NiBr_2$, NiI_2, $(Et_4N)_2NiCl_4$, $(Et_4N)_2NiBr_4$, and $(Bu_4N)_2NiI_4$. This list of rather colourful crystalline solids was extended with compounds from Group 2 that are promising future thermochromic materials with iodide and phosphine coordination ($NiI_2(PPh_3)_2$) and all S-coordination as in the $Ni(iPrDt^0)_2(BF_4)_2$ bisdithione and $Ni(S_2C_2Ph_2)_2$ bisdithiolene complexes. Group 3 samples were a series of blue and tan coloured thermochromic films that are consistent with the commercial formulation of Suntuitive interlayer (Figs.2A and 2B). Group 4 samples were model solution mimicking the function of commercial samples (Figs.2C). The darker coloured samples in Fig.2 correspond to the high temperature form of the samples.

The composition of the blue-coloured film as shown in Figures 2A and B is as follows: $NiBr_2 \cdot 2H_2O$, 2-butyl-2-ethyl-1,3-propanediol (BEPD), Bu_4NBr, Bu_4NI, 1-pentyl-1H-benzimidazole, antioxidant, plasticizer in Mowital B75H polyvinylbutyral polymer (PLEO-6). The solution samples in Figure 2C has the composition of $(Bu_4N)_2NiI_4$, Bu_4NI, 4-(3-phenylpropyl)pyridine, 2-butyl-2-ethyl-1,3-propanediol, and trace amounts of PPh_3 to minimize I_2 formation in γ-butyrolactone.
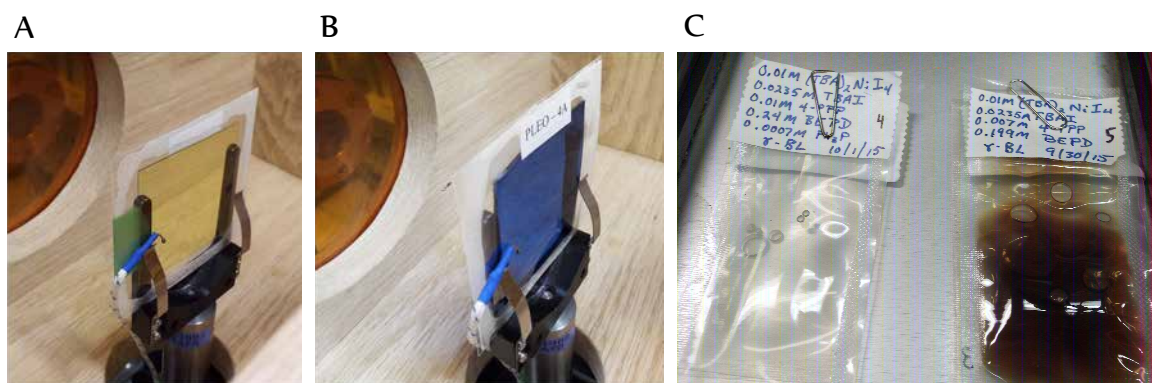
Fig.2. Commercial samples (A and B – bromide containing films) and solution model samples (C – iodide containing solutions).

Results and Discussion:

Reference spectra. The hexa- vs. tetracoordinate Ni(II) complexes with varied [NiO$_6$] versus [Ni(Br/I)$_{3,2}$(N)$_{1,2}$] coordination environments provided a set of experimental handles due to the presence of a rich and also greatly different spectral features in both the XANES and EXAFS regions as shown in Figure 3. The nickel K-edge spectra clearly show discernible features in the pre-edge (8327–8333 eV) and rising-edge (8335–8345 eV) regions that can be used in principal component analysis of the thermochromic film and model solution samples. The tetrahedral complexes show intense pre-edge features as expected from the lack of centrosymmetry and thus the appearance of 3d/4p orbital mixing. The rising-edge features displays well defined, although not resolved features that are due to charge-transfer states in these highly covalent compounds. The Br K-edge spectra also show the appearance of pre-edge features that are weak for the (Bu$_4$N)$_2$[NiBr$_4$] and stronger for (1-Et-BzImi)$_2$NiBr$_2$ complexes. These spectral changes are due to the mixing of ligand (Br 4p) character with the electron holes of the Ni d-manifold. Normally the Br 1s→3d excitation should not be visible; however, due to the covalent Ni-Br bonds, the Br 4p character appears in the unoccupied Ni d-manifold. Despite that BL14B2 of SPring-8 gives the most resolved spectra at the iodine K-edge compared to our experience at other hard X-ray beamlines, we were unable to use this ligand K-edge for quantitative analysis.

In addition to the rich XANES region, the room temperature EXAFS features can also be correlated with the coordination environments changes (Figure 3). However, one needs to be careful with the quantitative analysis of these spectra, since as the temperature increases the thermal fluctuations reduce the scattering intensities and enlarges the large Debye-Waller factors.
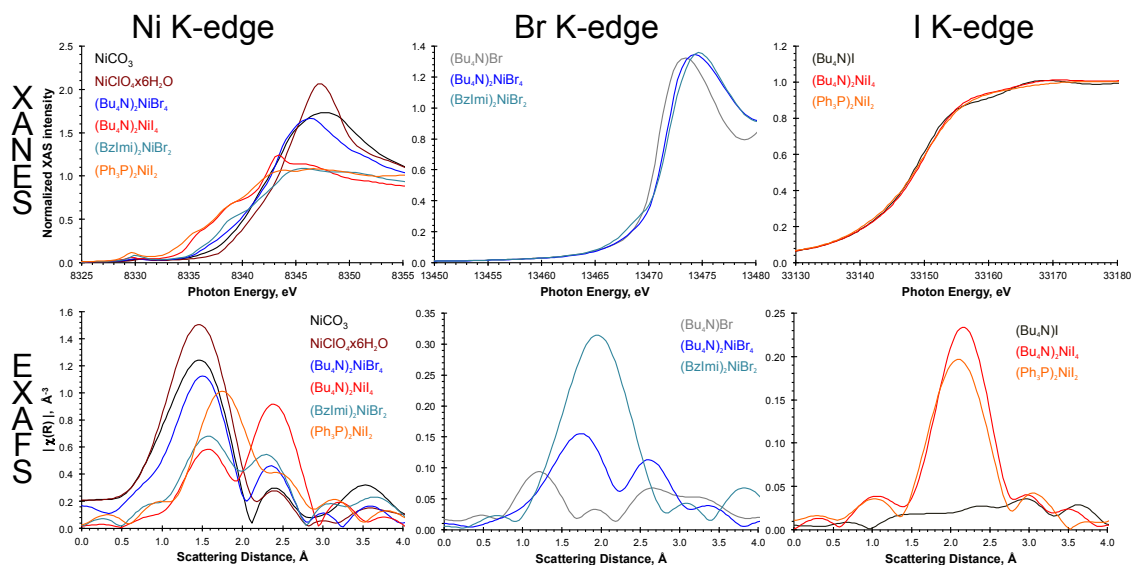

Fig.3. Comparison of multi-edge XANES and EXAFS spectra for the Ni reference set of the thermochromic films and model solutions: NiCO$_3$, Ni(ClO$_4$)$_2$x6H$_2$O, (Bu$_4$N)$_2$NiBr$_4$, (Bu$_4$N)$_2$NiI$_4$, (1-ethyl-benzimidazole)$_2$NiBr$_2$, NiI$_2$(PPh$_3$)$_2$; all spectra were obtained at room temperature.

Polymeric films and model solutions. The industrial collaborator, Pleotint LLC, provided 13 different films and 6 different solution samples. The presentation of results obtained for each of these samples goes beyond the scope of this report. Therefore, Figure 4 only presents typical results for the Ni K- and Br K-edges obtained for an actual commercial film. Resolutions limits the use of I K-edges for comparative analysis, therefore, no data were collected for analogous tan coloured film. It is also important to highlight that the large background of heavy elements (bromide and iodide counter ions) provided technical limitations of the transmission measurements. We anticipate that the use of fluorescence detection would provide a workaround for these limitations.

The XANES spectra in Figure 4 show the clear presence of a single isosbestic point at around 8343 eV as the $[NiO_6]$ coordination environment with high intensity white line and low intensity pre-edge feature converts into a mixture of four coordinate species that corresponds to $[NiBr_4]^{2-}$ and $[(1\text{-pentyl-benzimidazole})_2NiBr_2]$. Spectral deconvolution can be carried out to obtain estimates for the relative ratios. The corresponding EXAFS spectra also show the disappearance of the short Ni-O scatterer and the appearance of the longer Ni-Br scatterer at around 1.5 and 2.2 Å, respectively, without phase shift correction. In parallel, the Br K-edge (right hand side of Figure 4) showed a much smaller change, which is primarily due to the excess bromide anion dissolved in the polymer matrix as required by the Q, reaction quotient in Eq.(1). However, a less resolved isosbestic point can also be recognized that is an indication of a two state system. The increase of spectral intensities at around 13467 eV unambiguously indicates the formation of Ni-Br bonds, which give rise to a pre-edge feature.
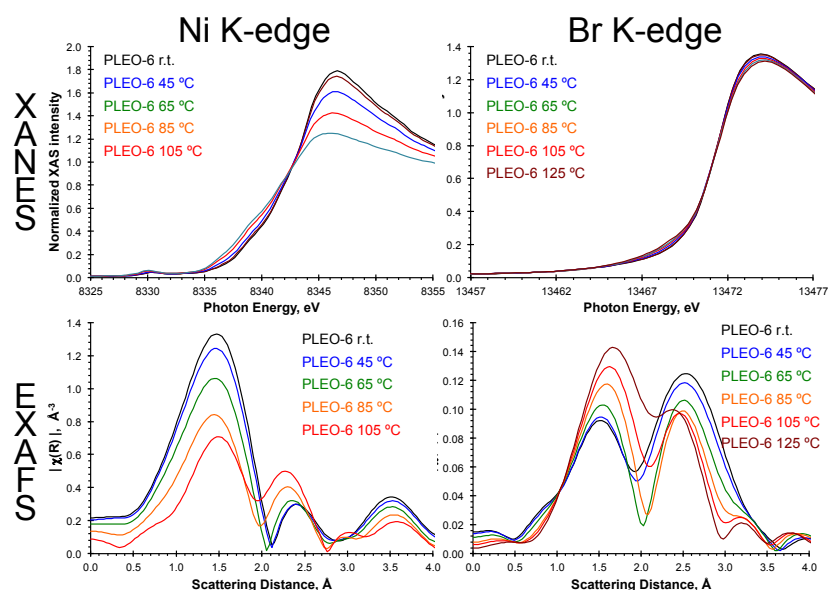

Fig.4. Temperature dependent XANES spectra at the Ni K- and Br K-edges for the commercial thermochromic blue film (PLEO-6 – see Experimental Section for composition information).

Interestingly the EXAFS spectra show drastic changes as the shorter scatterer at around 1.5 Å gaining, while the longer at around 2.5 Å loosing intensities. This can be rationalized by the formation of a mixture of complexes in the background of free bromide anions.

Next Steps :

The above described spectroscopic features and the expected compositional changes from the sample preparation allow us to set up molecular dynamics classical force field simulations for the actual 3D structural description of the thermochromic films and model compounds. The local environment of the chromophore Ni complexes will be refined with spectroscopically calibrated density functional theory to describe the spectroscopic features and in turn the thermodynamics of the thermochromic process. Having a unified theoretical model that can describe both the color and the thermodynamics of the entire system will be essential in optimizing existing and designing new interlayers that can be produced at lower cost or contain only a single layer. Furthermore, additional reference data collected at the soft X-ray beamline of SSRL (Stanford, USA) during the January 2016 run provides the complete electronic structure information for the reference compounds. This is essential in calibrating the level of theory for the quantum chemical simulations and thus eliminating a major uncertainty in computational modelling.

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