Elemental areal density calculation and oxygen speciation for flat glass surfaces using x-ray photoelectron spectroscopy

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ABSTRACT

The elemental composition of multi-component glass surfaces is often insufficient for understanding the effects of surface treatments on properties. For this reason, a data analysis protocol has been developed to quantify the areal density of elements and to determine the oxygen speciation on glass surfaces by X-ray photoelectron spectroscopy (XPS) for flat glass surfaces on which other methods such as optical spectroscopy and thermal analysis cannot be applied due to their low surface area, surface contamination, insufficient signal, etc. Various oxygen species (hydroxyls, non-bridging oxygen, and bridging oxygen) are distinguished and quantified using a simple workflow involving the determination of accurate elemental relative sensitivity factors, adventitious hydrocarbon contamination correction, and the conversion of the corrected elemental glass composition to areal elemental density. The areal density of oxygen species is obtained by a standard glass model based stoichiometry approach and compared with a constrained peak fitting of the O 1s photoelectron spectrum. The data analytical protocol is first verified with a silica glass, and then applied to pristine re-melt surfaces and acid-leached surfaces of commercial multi-component silicate glasses. XPS analysis revealed that upon leaching, significant repolymerization of network oxygen is observed in the calcium aluminosilicate glass surface in contrast to the lack of restructuring in the soda-lime silica glass surface.

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1. Introduction

Commercial applications for monolithic glasses include displays, windows, and bottles. Surface strength of these products is dictated by its flaw distribution and stress corrosion, which is known to be intimately connected to the glass structure and its modification due to the local environment [1]. It is desirable to correlate changes in strength with glass structure, specifically the network connectivity [2]. For example, in multicomponent silicate glasses, the network connectivity is dependent on glass composition and thereby, the distribution of network-formers such as silicon and oxygen, and network-modifiers such as alkali and alkaline-earth elements. The strength of glass is dependent on the weakest link in the structure (chemical flaws) such as broken network sites created by network-modifiers (non-bridging oxygen, NBO) and stress corrosion due to water (hydroxyls, OH) [3,4]. Therefore, the ability to quantify the areal density of NBO and OH as well as oxygen in the polymerized network, also known as bridging oxygen (BO), in glass surfaces can facilitate a quantitative structure-based approach to the study of the strength of glass surfaces. The areal density of these species at the surface is an important variable that can provide insight on the interaction of water and other molecules with the glass surface.

In industrial applications where the glasses come into intimate contact with another material, for example polymeric or organic-inorganic coatings, the interaction between the glass surface and the material has to be controlled for the intended performance [5]. The application of such coatings often requires the exposure of glass to an acidic medium, which is known to modify multi-component glass surfaces by leaching of network modifiers and formation of a silica gel-like layer [6–8]. The adhesion of coatings on a glass surface is directly connected to the chemical reactivity of the terminal glass surface (distribution of OH and NBO) [5,9]. Therefore, it is critical to determine the number of surface reactive sites to understand surface chemistry as it pertains to adsorption, wetting, and adhesion of materials on glass surfaces.

Typically, investigations into the surface chemistry of materials are conducted on high-surface area forms such as powders or fibers. These objects give a large surface area for optimal peak-to-noise ratio during characterization with infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and other analytical methods [10–14]. However, these techniques do not provide sufficient signal for surface reactivity studies on low surface area glasses. In order to apply these techniques to flat glass samples, one may choose to crush the glass into powder. However, it is not appropriate to compare crushed glass powder and monolithic cast glass as the surface chemistry

of a frozen melt surface is significantly different from a fractured surface [15].

When the glass surfaces of interest are monolithic, in the form of plates or slides, techniques such as X-ray photoelectron spectroscopy (XPS), specular reflectance spectroscopy (SR-IR), attenuated total reflectance spectroscopy (ATR), and sum-frequency generation spectroscopy (SFG) spectroscopy are used to study glass surface chemistry. Among these, XPS is the only technique that can provide quantitative information on the chemical states of elements such as oxygen (OH, NBO, BO) [16–18]. XPS analysis results can be refined to extrapolate areal density of surface sites using a few simple assumptions including surface structure, density, and spatial homogeneity in elemental distribution and oxygen chemical states. The areal surface density of sites via XPS analysis can be used in conjunction with results from other spectroscopy techniques (IR and SFG) to gain a better understanding of glass surface reactivity and site speciation [19]. Quantification of surface hydroxyls on low-surface area materials such as oxides or metal foils has been conducted using XPS [20,21]. However, these studies relied on the peak-fitting of high-resolution spectrum of oxygen 1s photoelectron to quantify OH, NBO, and BO, which is subject to a few potential drawbacks such as insufficient spectral processing, user bias and lack of verification of peak fitting results [22]. These factors complicate the quantification of surface hydroxyls in low-surface area studies if sufficient care in data analysis is not taken.

In this study, the analytical protocol for the quantification of surface hydroxyl species is developed using the anion-cation stoichiometry in the glass surface composition. The data analysis protocol presented here is a straightforward, single-technique approach for determining the surface areal density of elements and sites. The only prerequisites for this analysis are the determination of accurate elemental relative sensitivity factors and the correction of adventitious hydrocarbon contamination to obtain the actual glass surface composition, which is modified from the original study to include correction of carbonyl and acid groups in addition to alkyl groups [23]. Then, the elemental concentrations in atomic percentage (at.%) are converted to the areal density in atoms/nm^2 through a modification of the methods established by Iler and Sprenger [24,25]. Finally, the areal densities of BO, NBO, and OH in the top 10 nm region of the surface are calculated based on oxide stoichiometry. Silica glass samples were used to develop and verify this analysis protocol due to the availability of elemental and surface hydroxyl areal density data by other methods [24,26,27]. Then, the technique is applied to investigate the effects of acid leaching on the surface sites of commercially available multicomponent E-glass (boron-free, fluorine-free calcium aluminosilicate glass) and bottle glass (soda lime silica glass). A compositional dependence for surface repolymerization upon leaching is revealed after consideration of the areal density of oxygen species, which could not be obtained via the O 1s spectral analysis.

2. Experimental procedure

2.1. Materials

Fused quartz was obtained from Technical Glass Products (Painesville Twp., Ohio). The glass surfaces were first rinsed with ethanol and then UV/ozone cleaned for 30 min before usage. E-glass cullet was provided by Owens Corning (Ohio). The pellets were re-melted in a platinum-gold crucible at 1400 °C. Upon cooling, the glass was popped out of the crucible to preserve the fresh melt surface. Soda-lime silicate glass bottles were provided by Owens Illinois (Ohio). The bottles were crushed and re-melted in a platinum-gold crucible at 1250 °C.

2.2. Surface treatment

The re-melt E-glass and bottle glass surfaces were cleaned by UV/ozone and were not exposed to any solvents for cleaning. The leaching of the re-melt surfaces was performed using a pH 1 solution with HCl at 90 °C for 24 h. The leached surfaces were rinsed with DI water for an additional 10 min before drying by compressed N$_2$ and cleaning by UV/ozone. The fractured E-glass surface was created in the air immediately preceding the insertion into the analytical instrument to minimize hydrocarbon contamination.

2.3. X-ray photoelectron spectroscopy

A Kratos Analytical Axis Ultra spectrometer (Chestnut, NY) fitted with a monochromatic AlKα (1486.6 eV) X-ray source was used to characterize the samples. To minimize charging of the surface, samples with appropriately small lateral dimensions were wrapped with aluminum foil, mounted with conductive carbon tape and a low-energy electron flood gun was employed during the data acquisition. Survey scans and high-resolution narrow binding energy range scans of the O 1s, Na KLL, Ca 2p, Mg KLL, K 2p, C 1s, Si 2p and Al 2p peaks were conducted at 80 and 20 eV pass energies, respectively, at three random sample locations. The binding energies of all elements were corrected with the adventitious alkyl peak assigned binding energy of 285.0 eV. The curve fitting of O 1s and C 1s photoelectron peaks were conducted with GL(35) line shape and a Shirley background. Constraints for full-width half-max (FWHM) and position of component peaks were implemented as needed.

Determination of accurate relative sensitivity factors (RSF) is necessary for the quantification of XPS results [28]. The RSF for C 1s was obtained using polydimethylsiloxane (PDMS). The RSFs for the elemental peaks used for determination of glass composition were attained by analyzing the air-fractured cross-sectional surface of reference glasses whose bulk composition were determined using X-Ray Fluorescence (XRF) [29]. Reference glasses were chosen based on the elements present in the glasses in this study. The RSF of Si 2p was assigned a value of 1.0. The RSF for O 1s, Na KLL, Ca 2p, K 2p, Mg KLL, and Al 2p was determined by forcing the ratio of the elemental concentration of that specific element to silicon from the XRF data to equal the ratio of the area under the peak for the corresponding photoelectron/Auger peak and Si 2p. The RSF values determined using this method ensures that the instrumental parameters (transmission function, incidence angle, spectrometer function, etc.) of the specific XPS used are accounted for during the compositional quantification.

3. Experimental results

3.1. Development of data analysis protocol

The presence of adventitious hydrocarbon contamination can obscure the real glass composition. The first step is the determination of the actual surface composition by conducting the hydrocarbon overlayer correction, which is described in detail elsewhere [23,29]. Once the hydrocarbon correction is done, the surface composition determined by XPS can be assumed to represent the elements homogenously distributed within the information depth of the technique, typically cited as 10 nm [30]. Using basic knowledge of standard glass structure and its model-based stoichiometry between network-modifiers (NM) and network-formers (NF), the speciation of oxygen can be determined. The speciation of oxygen under consideration in this study includes bridging oxygen (BO; Si-O-Si), non-bridging oxygen (NBO; SiO$^-$), and hydroxyl (Si-OH) for a silicate glass. In alkaline earth (M) aluminosilicate glasses where the alkaline earth oxide and alumina (MO/Al$_2$O$_3$) ratio is >1, aluminum is considered to be a network-former in the tetrahedral form with charge compensation from M^{2+}. In addition, the only hydroxyls in the surface of glasses with MO/Al$_2$O$_3$ > 1 are silanols (SiOH). The excess M^{2+} cations after charge-compensation of aluminum tetrahedral sites give rise to NBOs. The surface composition of the glass also provides the oxygen to network-former (O/NF, where NF = [Si] + [Al]) ratio. Glasses with O/NF > 2 contain NBO