

Use of FTIR reflectance spectroscopy to monitor corrosion mechanisms on glass surfaces

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Abstract

Fourier transform infrared (FTIR) reflectance spectroscopy was used to monitor corrosion mechanisms on the surface of lithium disilicate ($\text{Li}_2\text{O}-2\text{SiO}_2$) glass samples exposed to an aqueous solution for short times. The traditional mechanisms of glass corrosion were observed but a spectral feature was resolved that was previously unreported. This feature consisted of a peak suspected to result partially from a silanol ($\text{Si}-\text{OH}$) vibration in the region $800-1050\text{ cm}^{-1}$ that shifted and reappeared in a cyclic fashion throughout the corrosion process. The behavior of this peak tends to suggest that the creation and condensation of $\text{Si}-\text{OH}$ groups is the reaction responsible for causing the shift of the main $\text{Si}-\text{O}-\text{Si}$ and $\text{Si}-\text{O}^-$ peaks, a phenomenon which has previously lacked a detailed explanation.

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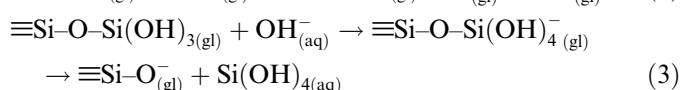
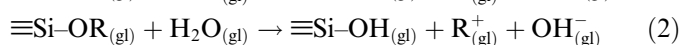
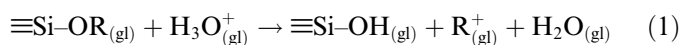
1. Introduction

Glass corrodes when in contact with an aqueous solution. Infrared reflectance spectroscopy has historically been a valuable technique for monitoring the effect of this type of corrosion on glass surfaces. The purpose of this work is to present experiments performed with a Fourier transform infrared (FTIR) reflectance spectroscopy technique to monitor static corrosion of lithium disilicate ($\text{Li}_2\text{O}-2\text{SiO}_2$) glass. This technique resolved a spectral feature not previously reported which may help to interpret the classical glass corrosion mechanisms.

Corrosion of standard laboratory and commercial silicate glasses occurs primarily by two mechanisms: leaching and network dissolution [1]. Leaching (or dealcalization) is the replacement of network-modifying constituent ions, such as alkali, with hydrogen ions from solution. Network

dissolution is the direct attack of the solution on the glass network. In either case, the result is the release of freed ions and glass network constituents into solution.

During the early stages of corrosion, leaching is the more active of the two processes. The exact mechanism for aqueous leaching has not been unequivocally determined for all glasses, but the leading theories state that water, in the form of H_3O^+ and/or H_2O , diffuses into the glass [2]. Upon encountering an alkali ion, the water species can react with the glass network so that the alkali is freed and a hydrogen ion (H^+) assumes the alkali's place. These two reactions are given in Eqs. (1) and (2) below, where R^+ indicates an alkali ion [2]. The reaction for network dissolution is given in Eq. (3) [2].



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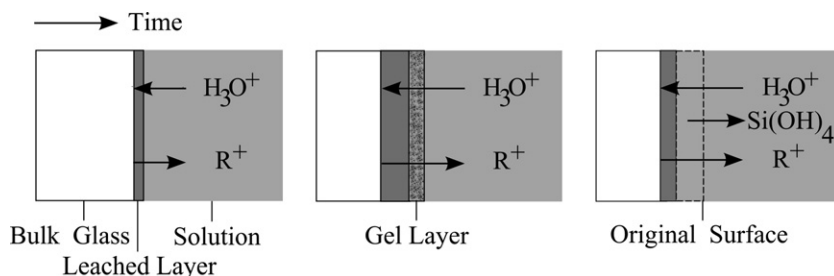
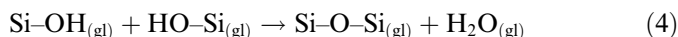


Fig. 1. Schematic illustration of the corrosion process over time.

As leaching proceeds, an alkali-depleted, SiO₂-rich layer is left behind. The interface between the bulk glass and leached layer proceeds into the bulk glass with time, and the leached layer grows in thickness. Leaching occurs most rapidly at the surface and slows as the leached layer grows in size, as both water species from solution and glass components have further to diffuse. The growth of the leached layer with time is illustrated schematically in Fig. 1.

The leached layer, rich in SiO₂ and deficient in alkali, is left with silanol (Si–OH) groups after leaching commences. The structure of the outer portion of the leached layer is often compared to that of a SiO₂ gel [3]. Phase separation between SiO₂ and water has been observed to occur [4]. Some theories of glass corrosion define this gel layer, or transformed layer, as a region distinct from the rest of the surface, even the leached layer [5]. The reaction associated with the formation of SiO₂ gel and phase separation is the condensation of the Si–OH groups, given in Eq. (4).



As H⁺ is depleted from solution by leaching, the pH of the solution increases and network dissolution accelerates

by Eq. (3). The etching effect of network dissolution on the surface, which causes SiO₂ to be dissolved into solution, is shown on the right in Fig. 1.

The use of infrared reflectance spectroscopy is an important alternative to traditional transmission or absorption infrared spectroscopy for studying glass corrosion in order to avoid difficult issues in sample preparation [6–8]. The FTIR reflectance technique uses the same basic principles, but is faster and more sensitive. It is useful for monitoring glass corrosion as it allows the use of room temperature and atmospheric pressure and it can be performed non-destructively directly on a sample surface.

The FTIR reflectance spectrum of a bulk glass surface is a product of the initial composition and structure of the glass. Fig. 2 shows the spectrum from both Li₂O–2SiO₂ glass and vitreous SiO₂. The vibration responsible for each major peak is labeled [6]. For the Li₂O–2SiO₂ glass, there is an additional peak due to the stretching of nonbridging oxygen (Si–O[−]) bonds that interact with the Li⁺ [6].

During the initial stages of corrosion, leaching depletes the exterior glass layer of alkali ions. This depletion causes the infrared spectrum from the surface to resemble that of vitreous SiO₂, causing the Si–O–Si peaks to shift in location

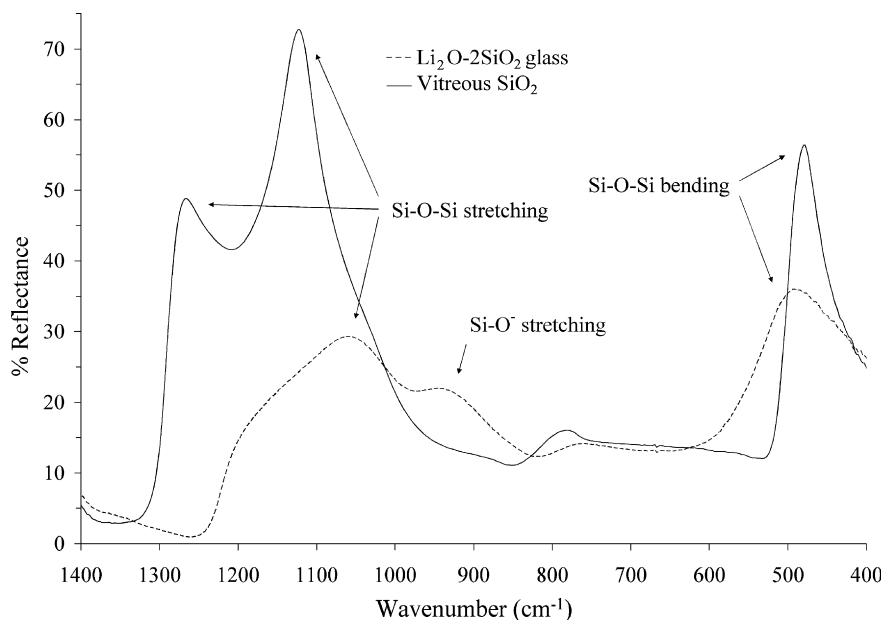


Fig. 2. FTIR reflectance spectra of Li₂O–2SiO₂ glass and vitreous SiO₂.

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