Concentration Profiles in the Surface Layer on Glass Electrodes by Argon–ion Beam Sputtering

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Summary The technique of ion-beam sputtering coupled with visible spectroscopy enables concentration profiles of sodium, lithium, calcium, hydrogen and other elements to be determined in the surface (gel) layer on glass electrodes after exposure to various electrolyte solutions.

INVESTIGATION of the detailed chemistry of the surface of glasses of the compositions used for glass electrodes is essential to the understanding of their electrochemical behaviour and of the origin of the acid and alkaline errors. Concentration profiles in the swollen surface (gel) layer have been studied by hydrofluoric acid etching coupled with chemical or radiotracer analysis.[1,2] Bach and Baucke[3–5] have made an important contribution by employing the argon ion-sputtering techniques used for thinning samples for electron microscopy,[6] with concomitant spectroscopic examination of the luminescence produced by the sputtering. Most of these authors' original work[3] was done without filters and the overall intensity was assumed to relate to lithium emission from lithium silicate glasses containing alkaline earth network modifiers. The full potentiality of the technique[4–7] can only be realised by using a monochromator to obtain individual concentration profiles of elements present in the glass or, more important, of foreign ions penetrating the gel layer from solution.

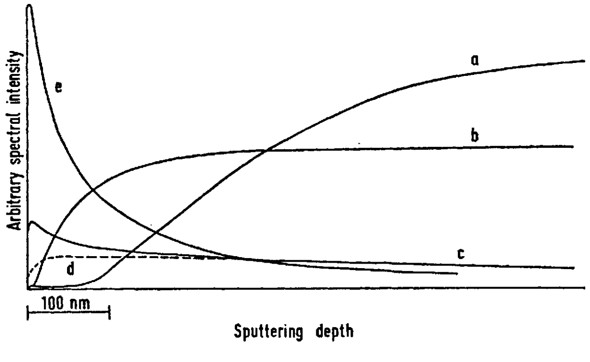

FIGURE 1. Concentration profiles in a soda lime silica glass (25–5–70 mol %) after soaking in 0·1M H_2SO_4 for 3 days. (a) Na (589 nm); (b) Ca (423 nm); (c) H (656 nm) immediately after exposure to low pressure; (d) as (c) but after exposure to low pressure for 1 h; (e) penetration of Li (671 nm) after soaking repolished specimens in 0·1M LiOH for 24 h.

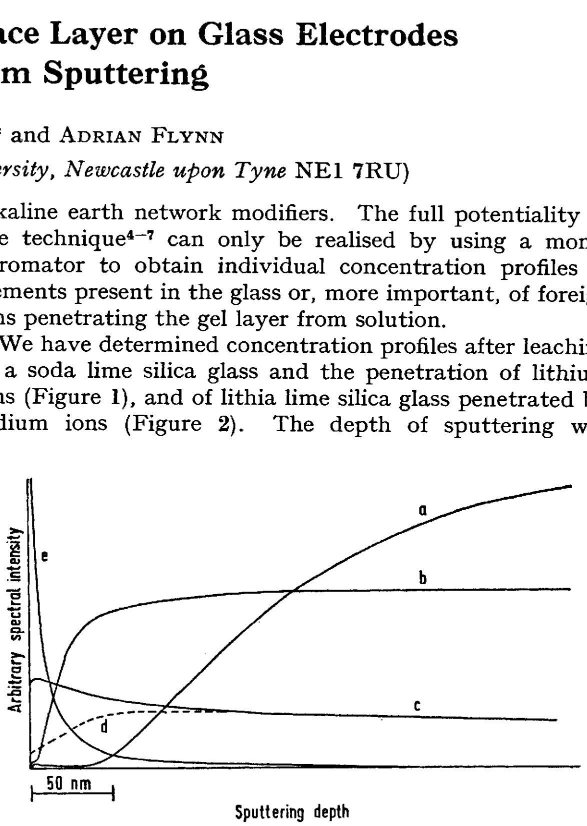

FIGURE 2. Concentration profiles in a lithia lime silica glass (20–5–75 mol %) after soaking in 0·1M H_2SO_4 for 3 days. (a) Li; (b) Ca; (c) H immediately after exposure to low pressure; (d) as (c) but after exposure to low pressure for 1 h; (e) penetration of Na after soaking repolished specimen in 0·1M NaOH for 24 h (spectroscopic analysis wavelengths as in Figure 1).

We have determined concentration profiles after leaching of a soda lime silica glass and the penetration of lithium ions (Figure 1), and of lithia lime silica glass penetrated by sodium ions (Figure 2). The depth of sputtering was estimated from inspection of the sputtered area and the weight loss. Further, hydrogen profiles can be determined, which was only previously possible using ^3H tracer. However, these H profiles vary with the time of exposure to low pressure (4×10^{-2} Pa) which causes loss of water from the gel layer. The lithia glass has a thinner gel layer on it, as judged by the H profile, than the soda glass in accordance with the fact that lithia glass absorbs only 1/9th as much water as do soda glasses.[8] The penetration of the Na^+ ions into the lithia glass is less than that of the Li^+ ions into the soda glass which accounts for the fact that lithia glasses show smaller alkaline errors.[9]

The removal of foreign cations from the glass surface can be followed after immersion in distilled water or a different electrolyte solution (for example most of the Li^+ ions comprising the ion profile shown in Figure 1 are leached out after 2 h in distilled water). This procedure closely parallels the practical use of glass electrodes and will be helpful in elucidating the nature of memory effects. The presence of large concentrations of other ions in solution, *e.g.* Mg^{2+} or Ba^{2+}, can lead to a reduction in the uptake of alkali metal ions, and hence lower errors at high pH.[10]

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