

Evidence of Adsorption of Hydrogen and Hydroxide Ions by pH-Sensitive Glass, and Chemical Potential Amplification

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A pH-sensitive glass was found to adsorb 51.6 H⁺ and 8.9 OH⁻ ions per nm² at pH 2.000 and p(OH) 3.500, respectively; the pH glass electrode potential could be amplified through capacitors connected in series.

Many investigators have attempted to explain the glass electrode potential ever since the electrode was created 80 years ago. The generally accepted ion-exchange mechanism failed to explain the origin of the potential and the acid and alkaline errors. Until recently, the glass pH electrode has been considered as a battery with a cell diagram involving redox reactions and a reversible thermodynamic equilibrium. The Nernst equation has been commonly used to relate quantitatively the potential to the logarithm of the ratio of unknown to known hydrogen ion activity (A_{H^+}); the role of OH⁻ ion in

potential development has been ignored. A new capacitor model proposes that the membrane electrode is considered as a capacitor instead of a battery.¹⁻⁴ It is based on the concepts of double layers, Boltzmann distribution, and surface charge density from ionic adsorption by the glass, and regards the potential as originating from electrode surface activity instead of solution activity.

In our experiments pH-sensitive glass (SiO₂ 70%, CaO 10%, Na₂O 20%) was ground (42-60 mesh) to obtain an average surface area of 0.0694 m² per g (measured by BET method). This ground glass (5 g) was soaked in concentrated HCl for 2 days at 50 °C with occasional stirring. It was then

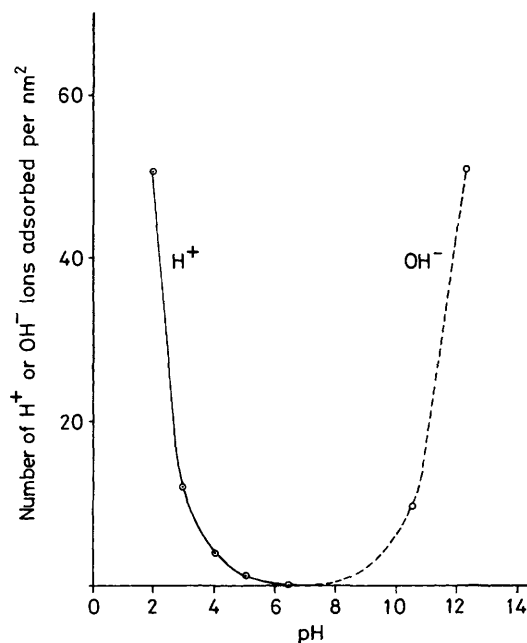


Figure 1. Adsorption of H⁺ and OH⁻ ions on a pH-sensitive glass surface.

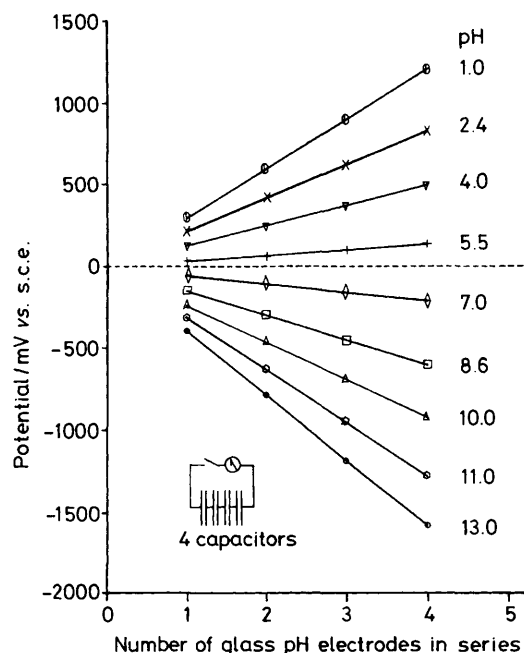


Figure 2. Chemical potential amplification with four glass pH electrodes in series.

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poured into a column which was washed with water until the filtrate was free from HCl (pH 6.5–7.0). To the air-dried ground glass was added 20.00 ml of unbuffered dilute HCl or NaOH solution of known pH value. After various times (*ca.* 40 min), the pH of the supernatant was measured with a Fisher Accumet 825 Mp pH meter. Doubly distilled water was used. The beaker was sealed with Saran wax paper during equilibration. For control purposes, similar experiments with ordinary glass (KIMAX) were also conducted. The results (Figure 1) indicate that at pH 2.000 and p(OH) 3.500 the pH-sensitive glass adsorbed 51.6 H⁺ and 8.9 OH⁻ ions per nm², respectively. At pH 6.2 (not 7.0) no significant amount of H⁺ or OH⁻ ion was adsorbed by the glass (isoelectric point). This agrees with results obtained by immersion with a tabular glass pH electrode.¹ Slightly lesser amounts of H⁺ and OH⁻ ion were also adsorbed by the ordinary glass. These results demonstrate that the glass surface exhibits a zwitterionic property (or amphoteric nature), enabling it to absorb the H⁺ and OH⁻ ions which are the source of the charges and the membrane potential development. These observations yield a new concept, that a glass pH electrode in acid solution is truly a pH electrode, but in alkaline solution, it should be regarded as a p(OH) electrode, since it actually responds to the OH⁻ ions.

It is doubtful whether 18 M KOH solution would yield the reported pH of 17.6.⁵ However the acid and alkaline errors of the pH glass electrode may be easily explained by the fact that the limited number of available active sites on the glass electrode surface cannot accommodate large amounts of H⁺ or OH⁻ ion at a linear rate.³

Figure 1 also shows that at pH 3.500 and p(OH) 3.500 the glass surface adsorbs equal amounts of H⁺ and OH⁻. A membrane electrode acting as a parallel plate capacitor should follow the capacitance law $E = q/C = (qd)/(\epsilon_0 kA)$.¹ Since C (specific capacitance), ϵ_0 (dielectric constant), k (permittiv-

ity), d (thickness), and A (area) are constant for a specific electrode membrane, E (surface potential) is dependent on q (surface charge). Also, E_{tot} resulting from series capacitor connections with a multimembrane electrode is the sum of each capacitor potential, ($E_{\text{tot}} = E_1 + E_2 + E_3 + E_4 \dots$).⁶ For the same solution the results with four multimembrane glass pH electrodes are shown in Figure 2. The values of ΔE (amplification) for pH 1.0 and 13.0 exceeded 1 V. This is a remarkable chemical potential amplification. Theoretically, an electrode of an unlimited number of membranes may be constructed with series connections, but there is a practical limitation. We note that an increase in positive potential is due to more adsorption of H⁺ ions, and an increase in negative potential to more adsorption of OH⁻ ions. This chemical potential amplification may offer applications; for instance, a simple voltmeter may be sufficient for pH measurement. Could the biological production of high voltage (electric eel) be based on the same principle? The results in both Figures 1 and 2 seem to provide strong experimental evidence to support the capacitor model for the membrane electrode potential.

Received, 25th March 1988; Com. 8/01223G

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