JOURNAL OF SOLID STATE CHEMISTRY **104**, 33–51 (1993)

Use of Alkali Glasses for the Preparation and Pressure Measurement of Alkali Metals, and Cesium Plate-out Levels on Transition Metals[1]

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Received October 29, 1992; accepted November 9, 1992

We have prepared pure Li, Na, and Cs films in ultrahigh vacuum apparatus by the electrolysis of alkali-oxide-containing glasses. Details of the procedure which enables precise amounts of alkali metal to be metered out are given. The alkali ions electrolyzed out of the glass cannot be replaced and the glass becomes progressively weakened. The construction and use of an electrochemical Cs pressure gauge is described. The gauge is an electrode concentration cell in which the electrodes display the activity differences. The electrolyte is any alkali-oxide-containing glass. When the Cs pressure to be measured is zero the gauge gives a base EMF which is different for each glass electrolyte used. Pyrex glass (4% Na_2O) works better than Cs_2O glass as the electrolyte because the base EMF for Pyrex is high. The EMF–pressure relationship is given by the Nernst equation and Cs pressures down to 10^{-17} Torr can be measured. The gauge has been used to assess Cs plate-out levels (i.e., equilibrium amounts deposited) on clean Ni at 0°C from Cs vapor at pressures below 10^{-13} Torr. Ni is an effective Cs getter, leaving little Cs in the vapor phase. Alkali-oxide-containing glasses approximate to Ohmic ionic conductors with a limited degree of electronic conduction. The glass characteristics alter with passage of current and some decomposition occurs with the formation of silica.

1. Introduction

The common commercial glasses are based on SiO_2 and contain Na_2O (up to about 16 wt%) and/or K_2O (up to about 11 wt%) in addition to many other oxides. The alkali oxides are added to reduce viscosity and softening temperatures. They disrupt the SiO_2 network by forming nonbridging O^- ions, while the alkali metal ions occupy holes in the network. As a result, alkali glasses are ionic conductors, often possessing appreciable electrical conductivity at elevated temperatures. Even commercial silica contains sufficient alkali impurity to render it conducting at hundreds of °C (*1*).

Interest in the conductivity of alkali

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[1] Dedicated to the memory of John Stuart Anderson and the way he inspired research.

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0022-4596/93 $5.00

glasses has centered on their ability to function as solid electrolytes in electrochemical devices such as pH meters and ion-specific electrodes for liquid systems, batteries, and fuel cells, and, more recently, a wide range of chemical sensors (*2*). Glasses are easily formed into convenient shapes for such purposes and effort has been directed at modifying their composition in order to increase electrical conductivity. For many purposes, however, high conductivity is not a prerequisite, e.g., the newer applications in microelectronics (*3, 4*) and in microionics (*5*), where good response times at low temperatures are readily achieved. In the following, we describe two uses to which the normal ionic conduction of heated single-alkali-oxide glasses of conventional type may be put. First we describe the preparation of up to centigram quantities of pure alkali metal films in ultrahigh vacuum apparatus by an electrolytic method. Then we describe the construction of an electrochemical pressure gauge capable of measuring extremely low alkali metal pressures. The gauge measures down to 10^{-17} Torr Cs and may be used to assess so-called Cs plate-out levels from the vapor phase onto transition metals. Finally we discuss the mechanism of electrical conduction in alkali oxide glasses.

2. Materials

The requirements for alkali glasses used to prepare alkali metal films electrolytically and to fabricate electrochemical pressure gauges are as follows. The glass should be capable of being formed into thimbles by the usual process of repeatedly blowing out a button of molten glass at the end of a tube. Thimbles are then joined to Pyrex glass tubulation for incorporation into a Pyrex glass (or metal) ultrahigh vacuum apparatus. The alkali oxide glass should therefore have a softening point that is about the same as that of Pyrex glass. This is so that thin-walled thimbles can be annealed along with Pyrex glass apparatus and be baked out while evacuated. In any case, during alkali metal preparation the alkali glass thimbles are evacuated and maintained at up to 420°C.

The alkali glass should contain 4 or 5 wt% of a single alkali oxide to be effective, and be free of other alkalis. Pyrex glass contains 4.2 wt% of Na_2O and no other alkali oxide; it is therefore very convenient for our purposes. A Li_2O glass and also a Cs_2O glass conforming to the requirements were mixed for us by Pilkington Bros. Ltd. using Analar grade reagents and Limoges quartz. The compositions of these glasses are given in Table I, together with their softening points and thermal expansion coefficients. The expansion coefficients are such that the Li_2O glass and the Cs_2O glass thimbles may readily be joined to Pyrex glass via graded glass seals (*6*) containing two or three intermediate glasses (*7*). One of our intermediate glasses, C9 (*8*), is included in Table I because it was used to construct an alkali pressure gauge.

Molten alkali salts were used as electrolytes. $LiNO_3$ of minimum purity 95 wt% was supplied by Koch–Light Labs Ltd. $NaNO_3$ was BDH Analar grade. $CsNO_3$ was to BDH GPR specification (98 wt% pure). For the pressure gauges, 99.98% pure Cs was supplied in ampoules by Koch–Light Labs Ltd. and fractionally distilled prior to use. Cs was also prepared *in vacuo* from chemical dispensers supplied by SAES Getters S.p.A., Milan.

3. Preparation of Alkali Metal Films in Ultrahigh Vacuum

Our preparation of pure alkali metal films is based on a method formerly used to introduce Na or K photocathodes into a glass photocell. The method, which is very old (*9*), has often been described in the literature (*10, 11*) and consists of the electrolysis of alkali-containing glass. One side of the glass

TABLE I

WT% COMPOSITIONS, SOFTENING POINTS, AND EXPANSION COEFFICIENTS OF THE ALKALI-OXIDE GLASSES USED

	Special Li_2O glass	Pyrex glass	Special Cs_2O glass	C9 glass (see Ref. (*8*))
Components/wt%				
Li_2O	4[b]	—	—	—
Na_2O	—	4.2	—	4
Cs_2O	—	—	5.0	—
K_2O	—	—	—	2
SiO_2	66	80.6	61.8	75
CaO	14	0.1	14.2	—
MgO[a]	6	0.05	9.5	—
B_2O_3	—	12.6	—	17
Al_2O_3	10	2.2	9.5	2
Softening point/°C	780	820	780	775
Thermal expansion coefficient/$10^{-6}K^{-1}$	5.5	3.3	5.0–5.4	4.25

[a] BDH Analar MgO, containing 0.3 wt% Na.

[b] Thimbles fabricated from 5% Li_2O glass developed vacuum failure more frequently.

is in contact with heated alkali salt melt (the anolyte) and a thermionic cathode is placed near the other side, which faces a vacuum. On application of electrical potential across the heated glass, alkali metal evaporates freely from the vacuum side of the glass. Burt (*12*) described the Na preparation as a procedure "which allows the vacuum to be electroplated with Na." We have developed a cell for the vacuum preparation of up to centigram quantities of alkali metals and used it to prepare pure Li (*13*), Na (*14–16*), and Cs (*17*) films for a number of years.

The electrolytic cell is shown in Fig. 1 and its characteristics are given in Table II. An alkali glass thimble, 5 to 8 cm long and 1.4 cm o.d., is joined to Pyrex glass tubing and mounted in a vacuum vessel on a reentrant seal. The thimble is extensively outgassed at 480°C by running the immersion heater in the empty thimble. Nitrate of the same alkali as in the glass is now added to the thimble and is maintained molten with the immersion heater. The quantity of nitrate melt is sufficient to fill the bottom third to half of the thimble. All the alkali nitrates decompose to nitrites above their melting points. As the temperature is further raised, the nitrites decompose to oxide with evolution of NO_2. A

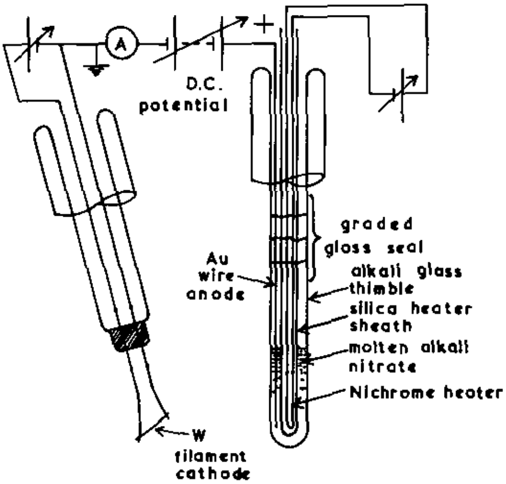


FIG. 1. Electrolytic preparation of alkali metal films. The reentrant alkali glass thimble (wall thickness 1 mm) is mounted in an ultrahigh vacuum apparatus with the W filament cathode 2–3 cm away.

TABLE II

CHARACTERISTICS OF ELECTROLYTIC CELLS FOR PREPARING ALKALI METAL FILMS

Alkali film	Typical dimensions in cm of thimble section filled with alkali salt	Measured conductivity of alkali glass/Ω^{-1}m^{-1}	Fused alkali salt in thimble with M.P./°C	Usual temperature of thimble during alkali preparation/°C	Usual DC potential applied across alkali glass/V
Li	4 long 1.4 o.d. 0.03 wall thickness	9.4×10^{-8} at 350°C; passing Coulombs can change by a factor 10	$LiNO_3$ 264 decomposed with $NO_2\uparrow$	350	1000
Na	3 long 1.4 o.d. 0.15 wall thickness	8.6×10^{-6} at 350°C	$NaNO_3$ 307 solid works too or $NaNO_2$ 271 decomposes with $NO_2\uparrow$	350	300
Cs	2 long 1.4 o.d. 0.10 wall thickness	1.2×10^{-8} at 350°C 1.8×10^{-7} at 420°C	$CsNO_3$ 414 best ($CsOH$ 272 melt attacks glass) (MeOOC.Cs 194 decomposes to give carbon deposits) ($CsCl$ 646 solid works too) ($NaNO_3$ 307 solid works too)	420	600

stabilized DC voltage supply is connected between an Au wire dipped into the melt and a W filament cathode situated in the vacuum vessel 2 or 3 cm from the thimble.

During operation, alkali metal evaporates from the alkali glass thimble and deposits on the walls of the surrounding vessel maintained at 0°C. The alkali ion current is determined by the thimble temperature, the voltage applied, and the filament emission current, i.e., the cathode temperature. The effect of varying voltage and emission current is shown in Fig. 2 for a Li source at 365°C. For each filament current there exists a saturation voltage beyond which no further current can be passed through the alkali glass. The maximum current probably obtains when all the electrons from the cathode arriving at the glass–vacuum interface serve to neutralize alkali ions. The best way to control the evaporating alkali flux up to this maximum is via filament temperature. Up to the saturation voltage, Li_2O glass behaves approximately as an Ohmic conductor. Fig. 3 shows closer Ohmic behavior of a Cs_2O glass thimble at 480°C. The saturation current passed through the alkali glass also depends exponentially on temperature. Either the thimble temperature or the filament emission current can limit the alkali flux so that altering one of these parameters may only be capable of lowering, not raising the

TABLE II—*Continued*

Alkali film	Largest current we drew from thimble/ mA cm^{-2}	Current stability	Typical alkali films that were produced in a 500 cm^3 glass reaction vessel	Thimble life
Li	0.028	≤5% fall over thimble life	5.4 C (0.39 mg) not visible	Vacuum failure and occasional implosion occurred due to hair-line cracks which developed in over half of 28 thimbles used; mainly after passing several C; No thimble survived with more than 3% of the Li^+ electrolysed. Thimbles of 5% Li_2O glass were more likely to fail.
Na	1.5	falls off slowly	6 C (1.4 mg) visible 36 C (8.6 mg) heavily opaque	It was established over the course of 37 runs that glass etched and developed hair-line cracks after passing about 70 C; replacement desirable after 50 C.
Cs	0.50	≤50% fall over thimble life	7.5 C (10 mg) visible	It was established over the course of 42 runs that thimbles slowly deteriorated in strength and shattered after roughly 15 C has been passed. 7.5 C was the safe limit. Only 0.6% of Cs electrolysed out was replaced from $CsNO_3$ melt. Pressure during Cs preparation never $>8 \times 10^{-9}$ Torr.

Alkali film	Notes
Li	—
Na	Thimbles can be used several times if $NaNO_3$ is washed out prior to outgassing—this avoids glass etching and breakage.
Cs	Ref.(*17*) gives a detailed description.

alkali flux. The thickness of the glass thimble wall is an important parameter too. Typical operating conditions for Li, Na, and Cs sources are given in Table II. Negligible electric current passes to the vessel wall, showing that alkali ions do not evaporate from the glass thimble. Thus the filament emission current never neutralized less than 98.5% of the Cs ions leaving a Cs_2O glass thimble. The electrolytic process accurately obeys Faraday's Laws so that precise amounts of alkali metal can be metered into the vacuum vessel. The Na introduced has been shown to be very pure (*12*, *18*, *19*). A quadrupole mass spectrum was run for Cs introduced when the background pressure was 8×10^{-9} Torr. No Na, O_2, or other unusual gases were detected. The comments column in Table II shows that the structural strength or tolerance to alkali ion removal during electrolysis is in the order Pyrex glass > Cs_2O glass > Li_2O glass. It

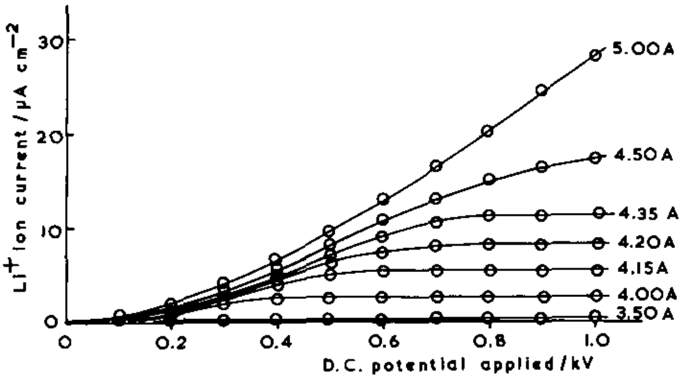


FIG. 2. Li^+ ion current as a function of the voltage applied to a Li_2O glass thimble for various filament currents. Thimble temperature 365°C, thimble wall thickness 0.3 mm.

was established that Cs continued to evaporate from a Cs_2O glass thimble if solid CsCl or molten $NaNO_3$ was used as the anolyte instead of molten $CsNO_3$. By fusing an Au or Pt anode directly onto the inside of the glass we were able to show that very small currents passed in the absence of any salt, but this current rapidly decayed.

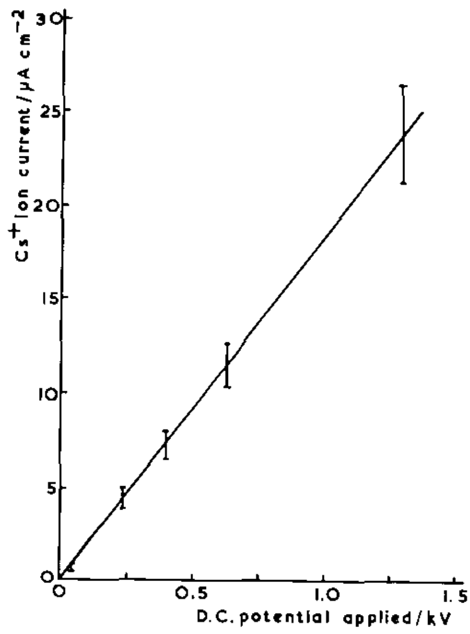


FIG. 3. Variation of Cs^+ ion current with voltage applied to a Cs_2O glass thimble at 480°C. Thimble wall thickness 1.0 mm.

4. Electrochemical Pressure Gauge for Alkali Metal Pressures

The need to construct an alkali-metal pressure gauge capable of measuring very low alkali partial pressures arises in both fusion and fission nuclear reactor technology. A Li pressure gauge could find application in the evolving fusion reactor but a more immediate need exists for a Cs pressure gauge in the design of gas-cooled nuclear fission reactors. The thrust in gas-cooled reactor design has been toward ever higher temperatures so that the release of fission products from the fuel into the coolant becomes progressively more of a problem. In the CO_2-cooled Magnox reactors fission product contamination is not a serious problem but in the high temperature gas-cooled reactor (*20, 21*) He replaces CO_2 and the core runs at 850°C to achieve high thermodynamic efficiency. At the same time the whole spectrum of U-235 fission products is picked up by the He coolant and transported around the coolant loop, where plate-out, i.e., deposition can occur, especially in the cooler parts.

The most serious fission product to be

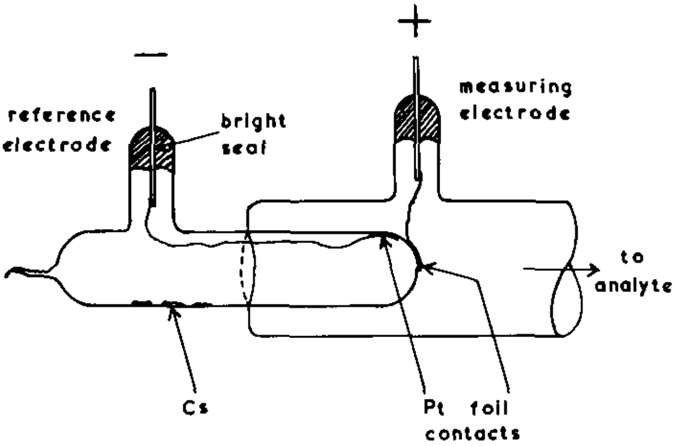


FIG. 4. Electrochemical pressure gauge for measuring Cs pressures down to 10^{-17} Torr. The gauge is constructed entirely of Pyrex glass because the glass electrolyte need not contain Cs ions.

deposited is Cs-137. It is a hard γ-emitter with a half-life of 30 years and presents serious problems for the maintenance and decontamination of loops. A need therefore exists to predict so-called plate-out levels of Cs under the working conditions and during the working life of a reactor. This can be done by measuring the adsorption isotherm for Cs on the material used for loop construction (usually stainless steel) and preparing a look-up table of plate-out levels as a function of temperature, time, and Cs pressure in the loop.

Our electrochemical pressure gauge for Cs pressure measurement follows the work of Kansky (*22*) who constructed electrochemical pressure gauges using special glasses of unstated composition. The basic idea is very simple but, as Kansky comments, difficulties arise which are entirely of an experimental nature. The gauge, Fig. 4, is an electrode concentration cell in which the electrodes display the activity differences. The reference electrode contains Cs, which sets up its vapor pressure at the temperature of the gauge. The measuring electrode is exposed to the unknown, low Cs pressure to be measured (the analyte). The electrolyte is Pyrex glass rather than Cs_2O glass (see below). The EMF E that is set up across the glass electrolyte is given by the Nernst equation and is a measure of the unknown Cs pressure P_{meas}:

$$E = \frac{RT}{F}(\ln P_{\mathrm{ref}} - \ln P_{\mathrm{meas}})$$
$$= \frac{2.303RT}{F}(\mathrm{pCs}_{\mathrm{meas}} - \mathrm{pCs}_{\mathrm{ref}}).$$

P_{ref} is the vapor pressure of Cs in the reference electrode of the gauge, $\mathrm{pCs}_{\mathrm{meas}}$ and $\mathrm{pCs}_{\mathrm{ref}}$ are defined in an analogous manner to pH, and R, T, and F have their usual meanings. The positive electrode is on the side of the gauge containing the lower Cs pressure which is to be measured. EMF–pressure plots calculated from the Nernst equation at 100°C to 200°C are shown in Fig. 5. The plots predict that E should rise to 1 to 2 V (depending on temperature) as P_{meas} falls to extremely low values. Although we found it difficult to make gauges that keep working, the predicted behavior has been obtained during gauge life (Section 5).

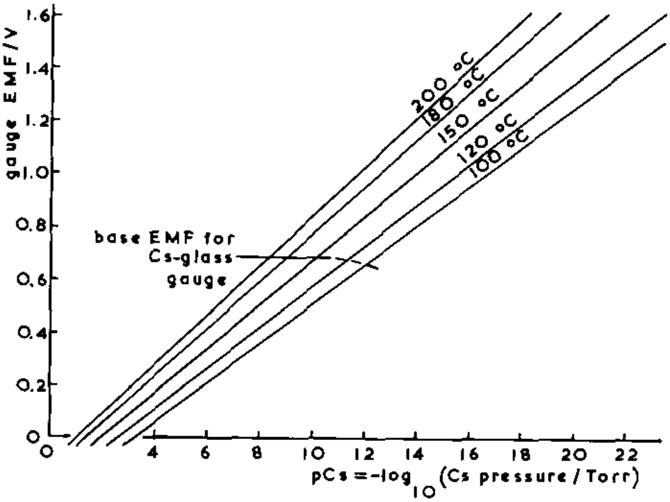


FIG. 5. Predicted EMF vs. Cs pressure for the electrochemical pressure gauge.

We first constructed Cs pressure gauges by sealing a Cs_2O glass disc into a Cs_2O glass tube and attaching each end of the Cs_2O glass tube to a Pyrex glass tube via a graded glass seal. Electrical contacts to each side of the Cs_2O glass disc were made with various combinations of thin Pt wire, thin Pt foil, and Pt paint. Most gauges broke after a few heating/cooling cycles. The more durable design shown in Fig. 4 was eventually adopted. A Cs_2O glass thimble (wall thickness about 1 mm) is joined to a Pyrex glass tube via a graded glass seal. Pieces of 0.05 mm Pt foil are flame welded to Pt wires and the foil is stuck to each side of the Cs glass thimble while the glass is soft. The Pyrex tube is then sealed into a wider Pyrex tube and the W glass seals are added. The W seal on the open or measuring electrode of the gauge (exposed to low Cs pressures) is the usual oxide seal but the W seal on the closed or reference electrode of the gauge (containing a few centigrams of Cs) is an oxide-free bright seal (*23*); this is because Cs attacks oxide seals above room temperature, causing them to leak.

Cs ampoules or Cs chemical dispensers were used to charge the reference electrode of gauges with Cs. Each gauge was first baked out to obtain ultrahigh vacuum. Cs was then flame-chased into the reference electrode and the reference electrode was sealed off. Gauges were mounted outside the main bake-out oven because Cs attacks bright W glass seals at our bake-out temperature of 320°C. Pyrex glass is eventually attacked too—all alkalis except Li are compatible with glass only below 250°C (*24*). Gauges were normally run at 180°C, chiefly to shorten response time (below). For this purpose the gauges were contained in a separate, small oven capable of maintaining gauges at up to 200°C. The equilibrium EMF developed by gauges was measured with a vibrating reed electrometer (Cary Instruments Inc., Model 401), with the preamplifier connected directly to the gauge. Gauges were carefully screened against electrical interference. Even so, EMF outputs were disturbed by electrical switching in the vicinity and by static electricity generated by manual or flame contact with adjacent, connected glassware.

After experimenting with gauges based on a Cs_2O glass thimble we discovered that Cs_2O glass was not necessary as the electrolyte. A gauge constructed entirely of Pyrex glass worked just as well. Indeed, all-Pyrex glass gauges are capable of measuring much lower Cs pressures than Cs_2O glass gauges (see Section 5), they are easier to make (no graded glass seal), and they last longer (the glass structure is more stable). All-Pyrex glass gauges were therefore adopted after the initial work with Cs_2O glass gauges. However, one gauge was constructed with a C9 glass (Table II) electrolyte so that the effect of electrolyte composition could be further investigated.

The measuring electrode of the gauges was attached to a 500 cm^3 Pyrex reaction vessel which formed part of a glass ultrahigh vacuum system. Cs was introduced to this vessel from Cs ampoules or Cs chemical dispensers and maintained at a set temperature for gauge calibration purposes. The vapor pressure of Cs was calculated from the formulae of Taylor and Langmuir (*25*), whose data still appear to be the best available and agree with later compilations (*24, 26*). For measuring Cs isotherms on Ni, the reaction vessel bore three side arms. One enabled Ni films to be evaporated onto the inside wall of the vessel. The second enabled Cs to be admitted electrolytically (see Section 3). And the third arm bore a W thermionic cathode which served both to admit Cs (Fig. 1) and to measure surface potentials by the diode method (*15*) for Cs adsorbed on Ni. For this purpose there was an electrical contact on the inner vessel wall. Prior to the admission of Cs, a Ni film was evaporated onto the inside wall of the reaction vessel to cover the glass (and simulate the inner surface of a nuclear reactor coolant loop). Cs pressure measurements therefore refer to equilibrium Cs pressures over a Ni adsorbent.

5. Cs Pressure Gauge Performance

All Cs pressure gauges developed an equilibrium base EMF E_0 when the pressure of Cs in the gauge reference electrode was zero. Characteristic E_0 values were measured for each gauge, both with the gauge joined to the ultrahigh vacuum system, and removed from it and open to air—no difference was noted. E_0 was also recorded at once during Cs pressure measurements if a leak occurred in the apparatus to which the gauge was attached. The variation of E_0 with temperature is shown for Pyrex glass, Cs_2O glass, and C9 glass gauges in Fig. 6. Below about 125°C the equlibrium time to reach a stable E_0 value increased, rising to about 20 min at room temperature. Above 125°C equilibrium E_0 values were rapidly attained. E_0 reached a maximum value for each gauge above about 125°C and E_0 values at 180°C are given in Table III. All E_0 values tended to be higher after heating cycles and this is reflected in the uncertainty limits. Gauges were maintained at 180°C for Cs pressure measurements to shorten the response time, to stabilize E_0, and to choose a convenient compromise between large EMF and low pressure.

Pyrex glass and Cs_2O glass gauges maintained at 180°C were calibrated by exposing the measuring electrode to Cs maintained at 77 K (V.P. zero), 195 K (V.P. 9.4×10^{-14} Torr), 273 K (V.P. 8.1×10^{-8} Torr), and 296 K (V.P. 1.1×10^{-6} Torr). The V.P. of Cs in the reference electrode was taken as 0.0352 Torr. With Cs at 77 K exposed to the measuring electrode E_0 was recorded. EMFs for both Pyrex glass and Cs_2O glass

TABLE III

BASE EMF RECORDED FOR GAUGES AT 180°C WITH NO CS IN THE MEASURING ELECTRODE

Gauge electrolyte	E_0 at 180°C/V	No. of measurements
Cs_2O glass	0.69 ± 0.09	8
Pyrex glass	2.15 ± 0.01	7
C9 glass	0.52 ± 0.02	2

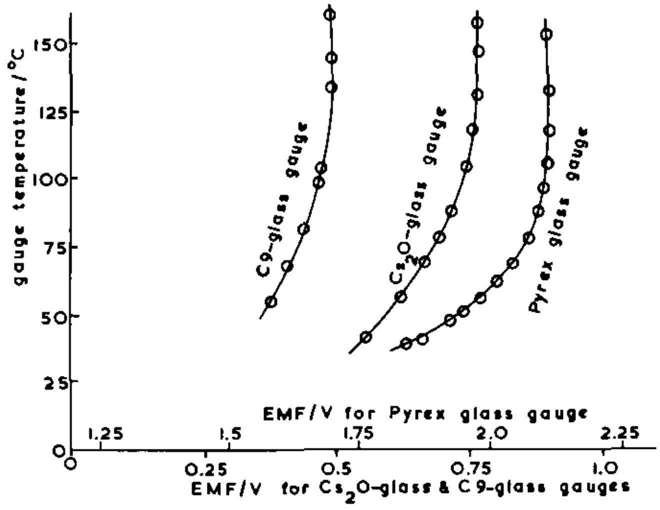


FIG. 6. Variation of base EMF with temperature for Cs_2O glass, Pyrex glass, and C9 glass Cs pressure gauges. There is no Cs in the measuring electrode throughout.

gauges agreed with theoretically predicted values (Fig. 5) to within 0.15 V at 195 K and to within 0.01 V at 273 K and 296 K. No correction was made for thermal transpiration because it only alters the EMF by tens of mV for Cs pressures below room temperature. Negative EMFs were temporarily recorded when Cs in the reaction vessel was gently flamed, raising the temperature to above 180°C. Although our Pyrex glass gauges were capable of measuring Cs pressures down to about 10^{-17} Torr, they often failed due to loss of satisfactory electrical contact with each side of the glass electrolyte.

Fig. 7 shows a successful low pressure Cs isotherm run on Ni at 0°C. A 35 mg Ni film was first evaporated in ultrahigh vacuum onto the inside wall of the reaction vessel maintained at 0°C. The film was then annealed for 1 h at 140°C to stabilize its structure. The film area was about 5 times the geometric area of the underlying glass. (This was established by Xe physisorption on similar films (*31*).) Cs was then dosed into the reaction vessel at 0°C using the electrolytic preparation method (see Section 3). At the same time the equilibrium Cs pressure was measured with a Pyrex glass gauge maintained at 180°C. Base EMF was recorded until about 5×10^{15} Cs atoms cm^{-2} of film substrate area had been admitted, when Cs pressures between 10^{-18} and 10^{-17} Torr started to be recorded. Gauge EMF then fell linearly with amount of Cs admitted while the calculated Cs pressure rose through 5 decades to 1.6×10^{-13} Torr. At this stage electrical contact with the gauge was lost.

To establish the coverage of Cs on Ni, the surface potential of Ni (negative change in work function) was also measured during Cs admission. We adopt the point at which the maximum surface potential is reached as that corresponding to monolayer coverage. Accordingly, all the Ni was covered when about 4×10^{16} Cs atoms cm^{-2} had been admitted. In Fig. 8 the EMF data are replotted as pCs (−log Cs pressure) versus number of Cs atoms admitted. Even at the highest pressure recorded when all the Ni is covered with Cs, the Cs equilibrium pressure is 10^{-4} of the vapor pressure of bulk Cs

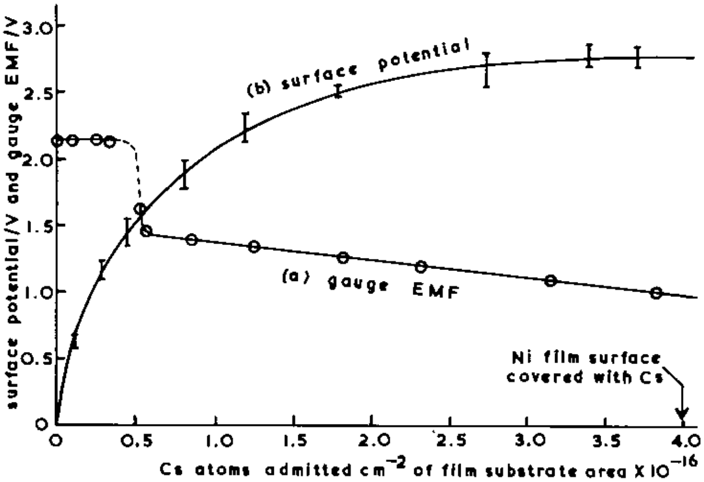


FIG. 7. Isotherms for Cs sorbed on evaporated Ni film at 0°C. Curve (a) EMF recorded on a Pyrex glass electrochemical pressure gauge maintained at 180°C as Cs is admitted. Curve (b) surface potential (negative change in work function) of Ni film as Cs is admitted.

at 0°C and only 10^{-13} parts of the Cs admitted remain in the vapor phase. The amount of Cs admitted may therefore be taken as the amount adsorbed and the data in Fig. 8 conform to a Temkin isotherm over a wide range of coverage.

6. Discussion of the Cs Pressure Gauge

Kansky (*22*) found that the Nernst equation was valid for his alkali pressure gauges up to EMFs of 1.5 V and Cs pressures in the range 10^{-3} to 10^{-19} Torr were measured. We also found that the Nernst equation correctly predicts gauge EMFs up to 1.5 V but 10^{-17} Torr Cs (5 cm^3 per Cs atom at 200°C) is a more realistic lower limit to the measurable pressure range.

The Cs pressure gauge we have described is a solid-electrolyte potentiometric sensor with Nernstian response. It represents one of a rapidly developing class of sensors

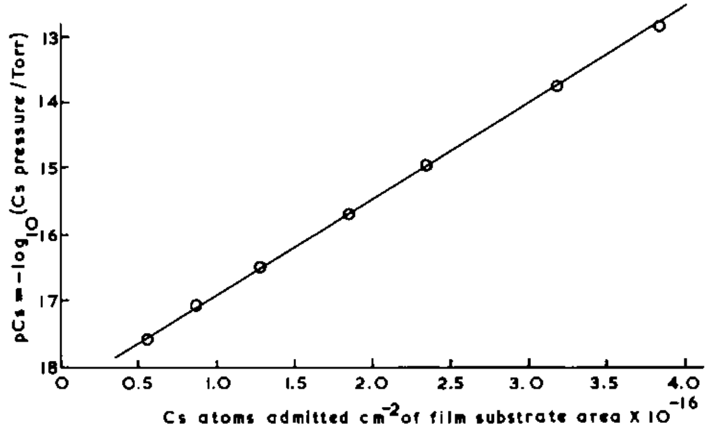


FIG. 8. Cs pressure over an evaporated Ni film at 0°C as Cs is admitted. Cs pressures were calculated from EMF readings using the Nernst equation.

which are capable of measuring gas pressures or concentrations (*2, 5*). Among these a Na pressure gauge has been described. It is capable of measuring Na pressures between 10^{-10} and 10^{-5} atm with a 10-min lag using β-Al_2O_3(Na), i.e., $NaAl_{11}O_{17}$ at 200–360°C, as the electrolyte. $Na_3Zr_2PSiO_{12}$, called NASICON, is another suitable fast Na^+ ion conductor. Candidate electrolytes for a Li pressure gauge are $Li_{14}Zr(GeO_4)_4$ and Li_3N. O_2 pressure gauges (*2, 27, 28*) reached commercial maturity many years ago. The solid electrolyte is CaO- or Y_2O_3-stabilized ZrO_2 (called CSZ and YSZ, respectively) held at 100–400°C and the reference electrode is either a metal/metal oxide mixture or Pt/air (oxygen pressure 0.21 atm). These gauges will measure oxygen pressures in the range 10^{-7} to 1 atm. Oxygen concentration gauges for monitoring the oxygen level in liquid Na are also well established (*28–30*). Based on Y_2O_3-doped ThO_2 solid electrolyte, they run at 500–600°C and are effective in the range 0.1–100 ppm. Solid electrolyte based sensors for many other common gases have been tabulated by Madou and Morrison (*5*). As we have found for the Cs pressure gauge, the solid electrolytes are not restricted to those which are conductors for the ions of the species to be monitored. For instance, Cl^- in $SrCl_2$ and F^- in $PbSnF_4$ have both been used for O_2 sensing in air and YSZ is a good pH sensor at 100°C. The only important factor appears to be the ability to sustain ionic conductivity with little corresponding electronic component at the operating temperature, which is invariably hundreds of °C to achieve practical response times.

Both Pyrex glass and C9 glass work as the electrolyte for a Cs pressure gauge although neither glass contains Cs^+ ions. Relevantly, we recall that Cs may be prepared from Cs_2O glass thimbles containing $NaNO_3$ as the anolyte. It therefore seems likely that any ionic conductor in which current is carried by alkali ions will work in an electrochemical Cs pressure gauge. Ideally such a conductor should possess good conductivity, stand high temperatures, be more durable, and be less likely to fail than glass. The conductor should also possess good vacuum qualities, resist Cs attack, and be capable of being shaped. A high-alumina silicate material such as sillimanite or mullite would fulfil these conditions if a high level of alkali ions could be built in. Alternatively, a more conventional fast ion conductor might be contained in a thin Mo or W alloy membrane which would resist all alkalis up to 1000°C. A nonalkali cationic conductor might also work as the electrolyte because Pyrex glass and C9 glass appear to function electrolytically in much the same manner as a salt bridge in a liquid concentration cell; it would only be necessary for Cs^+ ions to diffuse into the surface of such a conductor. As we have mentioned, the concentration of the most surprising analytes can be measured using chemically diverse electrolytes.

All our Cs pressure gauges produced a base EMF E_0 when there was no Cs present in the measuring electrode. E_0 rose with temperature, reaching a maximum value above about 125°C. This E_0 value tended to alter as the glass was aged by heating cycles. Glass coefficients of expansion are known to change in the same way, suggesting that E_0 variations are due to structural changes in the glass. For a Pyrex glass gauge the maximum E_0 (which would correspond to 6×10^{-46} Torr Cs) is probably due to electronic conductivity in the glass, electrons possessing a different chemical potential on each side of the glass electrolyte. In Section 7 we also conclude from other evidence that a small degree of electronic conduction occurs in our glasses.

The maximum E_0 for Cs_2O glass gauges was much lower than that for Pyrex glass gauges and corresponded to about 7×10^{-10} Torr Cs in the measuring electrode. Nevertheless we do not believe that E_0 is generated by Cs atoms drawn from the glass to set up a local pressure of Cs vapor. There are four pieces of evidence to oppose such a theory.

(i) The maximum E_0 for a C9 glass gauge corresponded to 6×10^{-8} Torr Cs even though C9 glass contains no Cs.

(ii) The maximum E_0 was unchanged on breaking the vacuum on the measuring side of Pyrex glass and Cs_2O glass gauges alike.

(iii) The amount by which E_0 falls for all gauges as the temperature is lowered to 100°C is only a small fraction of the EMF fall predicted by the Nernst equation.

(iv) E_0 for Cs_2O glass gauges did not rise continually, as might be expected if the surface Cs content of the glass slowly became exhausted. The rapid attainment of steady EMFs for all gauges above about 125°C also makes slow inevitable loss of alkali ions during operation unlikely.

Nevertheless we note that the Cs glass gauges gave the largest variation in maximum E_0 values and attribute this to variations in the glass composition at the measuring side occasioned during fabrication. We conclude that E_0 is due to electronic conduction in all gauges. Interplay between Cs pressure in the reference electrode, alkali ion mobility in the glass, and electronic conduction must account for the fact that electronic conduction does not increase exponentially with temperature.

Turning to the Cs isotherm on Ni, it is well known that an evaporated Ni film annealed at 140°C contains internal space between the crystallites. Thus the film area determined by Xe physisorption is many times greater than the geometric area of the underlying glass substrate onto which the Ni film is evaporated. In a study of Cs deposition on transition metal films (*31*) we have shown that Cs behaves in a liquid-like manner at 0°C and is imbibed by evaporated Ni films, filling up the internal space before completing the coverage of the film exterior. The surface potential initially rises (work function falls) when each dose of Cs is admitted to a Ni film but then falls again spontaneously. This recovery can take the surface potential back to zero for small initial admissions (and even to negative values on Fe films), only showing a cumulative rise for later Cs admissions.

These surface potential changes have a parallel in the thermal regeneration phenomenon (*32*) that occurs when oxygen is admitted to atomically clean Ni (or Fe) films, except that oxygen lowers the surface potential (work function rises) followed by a spontaneous rise. Such changes undoubtedly correspond to the oxygen penetrating into the lattice of the transition metal crystallites. The transition metals have very little solubility in alkali metals (*24, 33*) so that the spontaneous recovery effect in surface potential in the case of Cs must correspond to Cs flow into the film spaces and away form the exterior film surface which is "seen" in the diode method of measuring surface potential. About 4×10^{14} Cs atoms cm^{-2} are needed to form a monolayer on the *geometric* area of our Ni film substrate, whereas the surface potential technique indicated that monolayer coverage was not reached until about 4×10^{16} Cs atoms cm^{-2} had been admitted to the reaction vessel. At this stage Cs has "filled in" the film and the Xe physisorption area is measured to be the same as the geometric area of the film substrate (roughness factor unity). This is in contrast to the adsorption of Na (*14*) and Li (*13*) on transition metal films. Both Na and Li cover the transition metal crystallites evenly, so that monolayer coverage is achieved at 0°C after relatively small quantities of alkali metal have been admitted and transition metal films bearing adsorbed alkali retain a high area. Na is known, however, to penetrate the grain boundaries of stainless steel pipes (*34*) and pure Fe (*24*) above the melting point of Na and both heated Li and Na etch and leach stainless steel (*24, 35*). It therefore seems likely that Cs penetrates the grain boundaries of stainless steel at as low a temperature as 0°C and that an evaporated Ni film is not an unrealistic model for the wall of a nuclear reactor coolant loop at higher temperatures.

Cs plate-out levels have been measured on unclean stainless steel and carbon steels subjected to both static and flowing Cs pressures of 10^{-3} to 10^{-6} Torr at temperatures ranging from 343° to 735°C (*36*). A very high level of plate-out was noted and deposition of Cs, as measured by γ-counts, was still rising after many days. Sticking probability for Cs therefore appears to remain high well into the multilayer adsorption region. As we have found at lower pressures and temperatures, the log of Cs pressure was linear with amount of Cs taken up (Temkin isotherm).

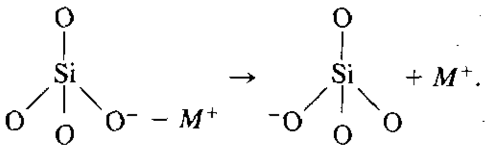
The long-term stability of photoemissive surfaces containing Cs in highly evacuated alkali-free environments may be assessed by measuring the equilibrium Cs pressure over the photoemissive surfaces. Kansky (*22, 38*) and Kansky and Jerič (*37*) have applied their electrochemical pressure gauge to the measurement of Cs pressures over Cs_xSb photocathodes from 10^{-14} Torr upwards and used the data to construct a phase diagram for the Cs–Sb system. The limiting sensitivity of their gauge was assessed at 10^{-20} Torr. Langmuir and Kingdon's surface ionization method (*39*) has also been used to measure extremely low Cs equilibrium pressures over photocathodes. A pressure of 10^{-14} Torr Cs has been measured over Cs_3Sb at room temperature (*40*), 10^{-16} Torr over Ag–O–Cs (*40*), and 10^{-17} Torr over a trialkali photocathode (*41*). The latter corresponds to a rate loss of $\sim 2 \times 10^3$ Cs atoms cm^{-2} s^{-1} so that it would take thousands of years to lose a Cs monolayer. These results show that the surface ionization method of measuring Cs pressures is as sensitive as the electrochemical pressure gauge. It is, however, an intrusive method and is also subject to interference from other nonalkali species in the ambient being sampled, especially at high pressures.

7. Mechanism of Electrical Conduction in Alkali Glasses

During the electrolytic preparation of Cs, most of the Cs flux produced is electrolyzed out of the glass without being replaced. Thus we have shown elsewhere (*17*) that less than 1% of the Cs ions removed from Cs_2O glass are replaced and the observation that Cs can be produced with solid or liquid $NaNO_3$ in the thimble supports this. We also recall that ion currents tend to fall slowly, indicating a depletion of current carriers in the conductor (as well as the formation of silica, see below). This loss of alkali ions leads to structural weakness in the glass and eventual collapse (Table II). A similar situation obtains for Li_2O glass during the preparation of Li despite the small size of the Li^+ ion. Pyrex glass, however, is longer lasting in the Na process (Table II) and stands higher current densities for longer periods. Anderson and Clark (*42*), for instance, using an external Pyrex thimble surrounded by $NaNO_2$ at 500°C were able to prepare 22 mg Na films in half an hour.

In the well-known crowding or ion-stuffing process to toughen glass, alkali ions in the glass surface are replaced. We find, however, that alkali ions may not be reintroduced to any appreciable depth after they have been electrolyzed out and no ions pass right through the glass. By the same token alkali glasses that do not contain Cs will work as the solid electrolyte across which EMF is developed in Cs pressure gauges. Negligible current is drawn from the gauge so there is little diffusion of alkali ions due to the electric field.

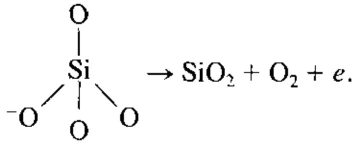
The question now arises as to how appreciable currents can be passed through our glasses during the electrolytic preparation of alkali metals. One way for this to happen (*17*) consistent with the difficulty of diffusing alkali ions *into* the glass is for negative charges on bound oxygen ions to transfer to the glass/anolyte interface as alkali ions *within* the glass diffuse away:



This mechanism, which reduces the transport number of M^+ ions to a little below unity, is tantamount to some electronic conduction within the glass. It may account for the base EMFs observed in alkali glass pressure gauges with no alkali present at all in the measuring electrode; viz., there is charge separation under influence of the M/M^+ electrode potential, the other electrode effectively being O/O^-.

Again, when appreciable current flows as in the electrolytic preparation of alkalis, negative charges on O^- ions will accumulate in the glass near the glass–anolyte interface. In this region the charges on O^- meet and are balanced (but not, in the main, discharged) by alkali or other ions from the salt in the thimble to an extent that varies with the nature of the salt.

In the absence of a salt, a back potential due to unbalanced charges rapidly develops as electrolysis proceeds and the conductivity of the glass is observed to fall quickly. On the other hand, a slow fall in conductivity observed when anolyte is present may be caused by the decomposition of some silicate groups resulting in the build-up of silica:



The negative charges released in this reaction are discharged at the glass–anolyte interface.

If the mechanism of ion transport we have proposed is correct, then an accumulation of alkali should occur at the positive glass surface in contact with anolyte during electrolytic preparation of alkalis. There may also be some loss of oxygen. At the same time the negative, vacuum-facing surface of the glass should undergo alkali depletion. These concentration changes have been confirmed by depth compositional profiles of electrolysed Cs_2O glass using X-ray photoelectron spectroscopy.

8. Depth Compositional Profiles by X-Ray Photoelectron Spectroscopy

A number of problems and restrictions arise in recording XPS spectra for alkali-containing glasses. Any tendency for alkali to diffuse out of the glass when placed in vacuum was avoided by cooling the glass to about −150°C. This precaution also obviates alkali migration due to Ar ion bombardment, X-irradiation, or electrical charge-up. The problem of charge-up was met by setting the electron flood gun current onto the binding energy plateau for Si (Fig. 9) where presumably the glass sample is electrically neutral, cp. (*43*), and the correct peak area/height will obtain. Another problem is presented by the low sensitivity in XPS of the lighter alkali metals.

In Table IV we collect some atomic sensitivity factors S for alkali metals, where

$$S = \frac{\begin{array}{c}\text{Height of alkali}\\ \text{XPS peak/mol\% of alkali}\end{array}}{\text{Height of O } 1s \text{ peak/mol\% of O}}.$$

S for the Li $1s$ peak is so low that we were unable to detect Li in our 5 wt% Li_2O glass (6.5 mol% of Li). The Li peak could just be seen in the spectrum for 13.7 wt% Li_2O Lindemann glass (12.1 mol% of Li) which we mixed according to Ref. (*44*). Na also has low S and the Na $2s$ and $2p$ peaks could not readily be identified in Pyrex glass for which the Na content (2.6 mol%) is near to

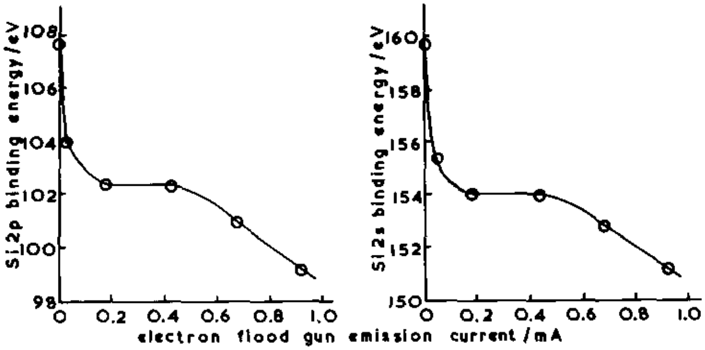


FIG. 9. Apparent variation of Si $2p$ and $2s$ electron binding energies with flood gun emission current for Spectrosil silica.

our detection limit in the 0 to 1000 eV binding energy range. On the other hand, S for Cs is high and our 5 wt% Cs_2O glass (0.78 mol% of Cs) gave large Cs $3d_5$ and $3d_3$ peaks. Cs_2O glass was therefore the only one that could be investigated by XPS. All spectra were recorded using a Vacuum Generators ESCALAB Mark II spectrometer.

A Cs_2O glass thimble was electrolyzed in a Pt crucible with molten $CsNO_3$ on each side of the glass. The 5.5 C passed were equivalent to about 8% of the indigenous Cs ions in the glass. The thimble was then smashed and a suitable fragment was briefly washed with water to remove $CsNO_3$, introduced into UHV, and cooled by passing liq-

TABLE IV

XPS ATOMIC SENSITIVITY FACTORS FOR ALKALI METALS AS PEAK HEIGHTS RELATIVE TO O $1s$ = 1.00

XPS peak	Material	Atomic sensitivity factor	Reference
Li $1s$	Lindemann glass	0.027	*(13)*
	BDH Analar Li_2CO_3	0.045	*(13)*
	Koch-Light Pure $LiNO_3$	0.090	*(13)*
	Empirical	0.030	*(46)*
	Not given	0.3	*(45)*
Na $2s$	Pyrex glass	0.025	*(13)*
	Soda glass	0.16	*(13)*
	BDH Technical Na_2SiO_3	0.11	*(13)*
	Empirical	0.18	*(46)*
	Not given	0.093	*(45)*
K $2p$ doublet	Soda glass	7.0	*(13)*
	Lead glass	<0.09	*(13)*
	Empirical	1.88	*(46)*
	Not given	2.1	*(45)*
Cs $3d_5$	5 wt% Cs_2O glass	54	*(13)*
	Empirical	10.6	*(46)*
	Not given	1.6	*(45)*
Cs$3d_3$	5 wt% Cs_2O glass	37	*(13)*
	Not given	1.2	*(45)*

uid nitrogen through the specimen manipulator. Each side of the glass was then depth profiled with the results shown in Fig. 10. The XPS peak areas that were followed for Cs, O, and Si are indicated. The etching time with 10 kV Ar ions was converted to depth etched away by measuring the weight loss after leaving the Ar ion gun on for 15.5 hr. During this time, 1.9 mg were etched from the glass specimen of density 3.0 g cm^{-3}. Peak areas taken directly from the spectra have been plotted in Fig. 10, rather than their conversion to atomic proportions. This procedure was adopted because atomic sensitivity factors are poorly known and variable, especially for glasses (Table IV). Furthermore, atomic proportions are not necessary for the present reasoning. A comparison of the profiles on the positive and the negative sides of the glass for each element demonstrates in a simple and direct fashion that:

(i) Washing with water depletes Cs and O to a depth of about 500 Å.

(ii) Between 500 and 2500 Å depth the Cs concentration on the negative side of the glass is about 20% less than on the positive side. This confirms that Cs is electrolyzed out of the glass without being replaced (and that Cs ions are current carriers).

(iii) Between 500 and 2500 Å depth the O concentration on the positive side of the glass is about 20% less than on the negative side. This confirms that silicate decomposition occurs on the positive side with evolution of O_2. There is also evidence that some quasi-free O ions have diffused from the negative side inwards during electrolysis.

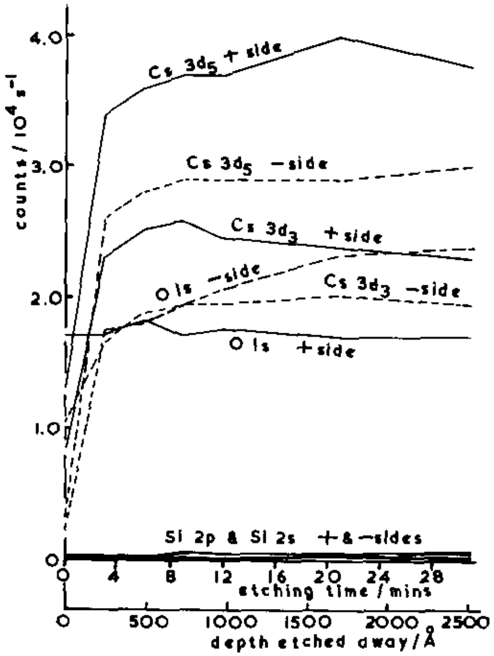


FIG. 10. Compositional depth profiles for Cs_2O glass after about 8% of the indigenous Cs^+ ions were electrolyzed out. Continuous line: positive side of glass. Broken line: negative side of glass. XPS atomic sensitivity factors have not been applied.

The binding energy of the Si $2p$ electron is generally ca. 0.5 eV higher in free SiO_2 than in an ionic network such as glass (*47*). This is less than the line width of the Al X-ray source and no peak splitting could be discerned. X-irradiation photolyzed glass samples, turning them brown, but no XPS evidence for the formation of free Si was obtained.

Heating Cs_2O-glass in air to 500°C for 15 hr greatly depressed all Cs XPS peaks to 2500 Å depth. Evidently Cs is readily lost by thermal diffusion.

Conclusions

1. Up to centigram quantities of pure Li, Na, and Cs may be prepared in ultrahigh vacuum apparatus by electrolyzing alkali-oxide glasses as elevated temperature.

2. Although alkali ions carry electric current through alkali-oxide glasses, the ions are not replaceable and the glass becomes structurally weak. There is also a limited degree of electronic conduction.

3. An electrochemical pressure gauge that uses Pyrex glass as the electrolyte is capable

of measuring Cs pressures down to 10^{-17} Torr. The EMFs produced accord with the Nernst equation.

4. The chemical nature of the alkali-oxide glass electrolyte does not affect the Cs pressure measured but it has considerable effect on the base EMF recorded for zero Cs pressure.

5. The adsorption of Cs on clean Ni at 0°C follows a Temkin isotherm up to at least 10^{-13} Torr. The Ni surface is an effective Cs getter, leaving little Cs in the vapor phase.

Acknowledgments

We are grateful to P. S. Irlam and R. Gaskell of Pilkington Brothers Limited, Research and Development Laboratories, for mixing the Li_2O glass and the Cs_2O glass to meet our specification. Thanks are due to N. Eslamdoost for preparing the XPS samples.

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