July 6, 1948. **G. A. PERLEY** **2,444,845**

PH-RESPONSIVE GLASS ELECTRODE

Filed May 9, 1946

7 Sheets-Sheet 1

FIG. 1

TABLE 1
GLASS COMPOSITION

No.	MOL PER CENT						AVERAGE MEGOHMS AT 25°C	pH ERROR, 25°C, 2 N SODIUM, 12.8 To 13.0 pH		
	R_2O		MO		OM	XO_2				
	Li	Cs	Ca	Ba	La_2O_3	Si		DAYS 2	MONTHS 6	YEARS 1-2
GR	23.7	1.7	6.3	1.5	1.9 (ZrO_2)	64.9	500	0.25	0.30	0.36
HC	23.4	1.7	6.3	1.5	2.9 (TiO_2)	64.2	780	0.12	0.13	0.15
GY	23.6	1.7	6.3	1.5	0.9 (ZrO_2)	66.0	850	0.23	0.25	0.28
HJ	24.9	1.2	6.2	1.5	4.3 (TiO_2)	61.9	450	0.25	0.50	0.55
HK	24.5	1.2	8.0	0.7	2.8 (TiO_2)	62.8	800	0.17	0.28	0.30
FK	24.2	1.4	9.9	0	0	64.5	1100	0.30	0.33	0.38
HD	22.4	1.2	11.9	0	0	64.5	2500	0.10	0.21	0.30
HP	22.4	1.2	14.8	0	0	61.8	11000	0.18	0.10	0.10
HI	25.2	1.2	6.3	1.5	2.8 (ZrO_2)	63.0	270	0.33	0.40	0.64
FY	23.2	1.7 (K)	11.4	0	0	63.7	4000	0.33	0.42	0.55
GP	22.9	0	14.1	0	0	63.0	1600	0.28	0.30	0.33
IA	22.4	1.6	5.9	5.5 (Mg)	0	64.6	2200	0.20	0.33	0.40
IC	23.2	1.6	5.1	2.8 (Sr)	0	67.3	1500	0.22	0.28	0.33
JZ	27	1	2	4	1 (Pr_2O_3)	65	160	0.13	0.14	0.32
KI	26	2	6	1	1 (Pr_2O_3)	64	700	0.13	0.14	0.14
KH	26	1	3	3	1 (Nd_2O_3)	66	300	0.25	0.30	0.40
KO	27	1	3	4	1	64	225	0.15	0.18	0.20
KT	25	1	3	5	1	65	550	0.15	0.15	0.15
KV	25	0	3	5	1	66	565	0.40	0.40	0.30
KX	25	1 (K)	3	5	1	65	800	0.21	0.25	0.25
KY	25	1 (Rb)	3	5	1	65	930	0.13	0.13	0.13
LB	25	1	3	5 (Sr)	1	65	590	0.23	0.20	0.20
LJ	26	1	5	5	0	63	550	0.20	0.30	0.51
LR	26	1	3	5	1	64	550	0.17	0.13	0.10
MG	25	1	0	7 (Sr)	2	65	1600	0.19	0.13	0.13
MH	25	1	0	7	2	65	1700	0.17	0.16	0.31
MN	24	2	4	4	3	63	4000	0.12	0.07	0.07
MO	26	2	4	4	1	63	1300	0.10	0.07	0.10
MP	27	1	2	6	3	61	300	0.15	0.15	0.15
MS	25	0	0	7 (Sr)	3	65	950	0.30	0.30	0.50
MT	25	0	0	7	3	65	600	0.20	0.22	0.20
MU	24	2	2	4	5	63	5000	0.30	0.28	0.10
MV	25	0	2	4	6	63	1600	0.30	0.30	0.35
MW	25	2	2	4	4	63	1500	0.10	0.06	0.10
NA	25	1	0	4	5	65	670	0.15	0.18	0.18
NB	25	2	2	5	3	63	1600	0.09	0.10	0.10
ND	25	2	2	3	5	63	1600	0.12	0.10	0.10
NE	25	1 (Na)	0	7	2	65	1800	0.40	0.50	0.53
NF	25	1 (K)	0	7	2	65	1300	0.30	0.45	0.50

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July 6, 1948. G. A. PERLEY **2,444,845**

PH-RESPONSIVE GLASS ELECTRODE

Filed May 9, 1946 7 Sheets-Sheet 2

TABLE 1 (CONTINUED)

FIG. 1 (CONTINUED) GLASS COMPOSITION

No.	MOL PER CENT						AVERAGE MEGOHMS AT 25°C	pH ERROR, 25°C, 2 N SODIUM, 12.8 To 13.0 pH.	
	R_2O		MO		OM	XO_2			
	Li	Cs	Ca	Ba	La_2O_3	Si		DAYS 2	MONTHS 6
NH	25	1	3	5	1	65	900	0.16	0.10
NI	25	1	0	7	6	61	2600	0.10	0.08
NK	25	2	0	8	2	63	2000	0.08	0.07
NL	25	2	0	6	4	63	1000	0.08	0.03
NM	25	2	0	4	6	63	1100	0.04	0.05
NS	25	2	2	6	2	63	1500	0.09	0.10
NT	25	2	4	4	2	63	1350	0.10	0.05
NU	25	2	6	2	2	63	1300	0.10	0.08
NV	28	2	0	5	2	63	80	0.12	0.07
NW	25	2	8	0	2	63	1200	0.09	0.10
NX	25	2	2	5 (Sr)	2	64	1500	0.09	0.12
NZ	28	2	2	2	2	64	65	0.15	0.30
OA	28	2	2	2	4	62	210	0.17	0.11
OB	28	2	2	4	2	62	200	0.10	0.11
OD	25	2	2	4	4	63	2000	0.13	0.05
OE	25	2	2	4	3	64	1000	0.13	0.08
OF	25	2	2	4	1	66	460	0.20	0.20
OG	26	2	2	4	2	64	450	0.07	0.07
OI	26	2	2	4	2 (Pr_2O_3)	64	450	0.07	0.10
OJ	26	2	2	4	2 (Nd_2O_3)	64	450	0.08	0.15
OK	26	2	2	4	2 (CeO_2)	64	480	0.10	0.16
PX	26	2	2	4	2 (TeO_3)	64	380	0.17	0.17
OS	26	2	2	4	2 (P_2O_5)	64	150	0.32	0.21
OH	26	2	2	4	2 (Co_2O_3)	64	2400	0.28	0.30
ON	26	2	2	4	2 (ZrO_2)	64	250	0.20	0.33
OM	26	2	2	4	2 (TiO_2)	64	280	0.10	0.35
PU	26	2	2	4	2 (Cb_2O_5)	64	210	0.16	0.35
OQ	26	2	2	4	2 (Ta_2O_5)	64	200	0.12	0.40
OP	26	2	2	4	2 (ThO_2)	64	280	0.12	0.40
OU	26	2	2	4	2 (As_2O_5)	64	190	0.40	0.46
OO	26	2	2	4	2 (UO_2)	64	300	0.25	0.47
OV	26	2	4	2	2	64	500	0.09	0.15
PA	26	0	0	7	3	64	360	0.10	0.14
PI	27	2	3	2	3	63	280	0.09	0.15
PL	28	2	0	5 (Sr)	2	63	180	0.10	0.14
PN	28	2	0	3	4	63	130	0.10	0.09
PO	27	2	4	0	4	63	325	0.12	0.16
PR	28	1	5	0	3	63	300	0.20	0.28
PP	28	1	0	5	3	63	200	0.09	0.10
PS	28	1	0	5 (Sr)	3	63	170	0.19	0.15
PT	28	2	0	3 (Sr)	4	63	170	0.11	0.16

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TABLE 2

FIG. 2 GLASS COMPOSITION VS. ELECTRICAL RESISTANCE

No.	MOL PER CENT						AVERAGE MEGOHMS AT 25°C	pH ERROR, 25°C, 2 N SODIUM 12.8 To 13.0 pH
	R_2O		MO		OM	XO_2		
	Li	Cs	Ca	Ba	La_2O_3	Si		DAYS 2
NK	25	2	0	8	2	63	2400	0.08
NS	25	2	2	6	2	63	1500	0.09
NT	25	2	4	4	2	63	1350	0.10
NU	25	2	6	2	2	63	1300	0.10
NW	25	2	8	0	2	63	1200	0.09
OF	25	2	2	4	1	66	450	0.20
OE	25	2	2	4	3	64	1000	0.13
OD	25	2	2	4	4	63	2000	0.13
OY	26	1	2	3	1	67	190	0.27
OG	26	2	2	4	2	64	450	0.07
MO	26	2	4	4	1	63	1300	0.10
OC	28	2	2	2	1	65	70	0.25
OA	28	2	2	2	4	62	190	0.17
NY	25	0	0	8	0	67	480	0.25
MZ	25	1	0	9	0	65	725	0.60
NJ	25	2	0	10	0	63	1300	1.50
NB	25	2	2	5	3	63	1600	0.10
NV	28	2	0	5	2	63	80	0.12

TABLE 3

FIG. 3 TYPE OF R_2O vs. SODIUM ERROR

No.	MOL PER CENT							AVERAGE MEGOHMS AT 25°C	pH ERROR, 25°C, 2 N SODIUM 12.8 To 13.0 pH	
	R_2O			MO		OM	XO_2			
	Li	Na	K	Ca	Ba	La_2O_3	Si		DAYS 2	MONTHS 6
PA	26	0	0	0	7	3	64	360	0.10	0.14
PB	0	26	0	0	7	3	64	150	1.33	0.80
PC	0	0	26	0	7	3	64	600	2.75	Dissolved
LZ	25	0	0	3	5	2	65	900	0.30	0.50
MA	0	25	0	3	5	2	65	250	1.15	1.40
MB	0	0	25	3	5	2	65	900	2.43	4.10

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July 6, 1948. G. A. PERLEY **2,444,845**

PH-RESPONSIVE GLASS ELECTRODE

Filed May 9, 1946 7 Sheets-Sheet 4

FIG. 4

TABLE 4

INFLUENCE OF CESIUM ON SODIUM ERROR, pH

No.	MOL PER CENT									AVERAGE MEGOHMS AT 25°C	pH ERROR, 25°C 2 N SODIUM 12.8 TO 13.0 pH
	R_2O		MO					OM	XO_2		
	Li	Cs	Be	Mg	Ca	Sr	Ba	La_2O_3	Si		Days ½
MI	25	0	7	0	0	0	0	3	65	115	2.51
MD	25	1	7	0	0	0	0	2	65	150	1.89
MQ	25	0	0	7	0	0	0	3	65	445	1.15
ME	25	1	0	7	0	0	0	2	65	880	0.93
MR	25	0	0	0	7	0	0	3	65	485	0.50
MF	25	1	0	0	7	0	0	2	65	1280	0.41
MS	25	0	0	0	0	7	0	3	65	810	0.30
MG	25	1	0	0	0	7	0	2	65	1655	0.13
MT	25	0	0	0	0	0	7	3	65	800	0.21
MH	25	1	0	0	0	0	7	2	65	1600	0.13

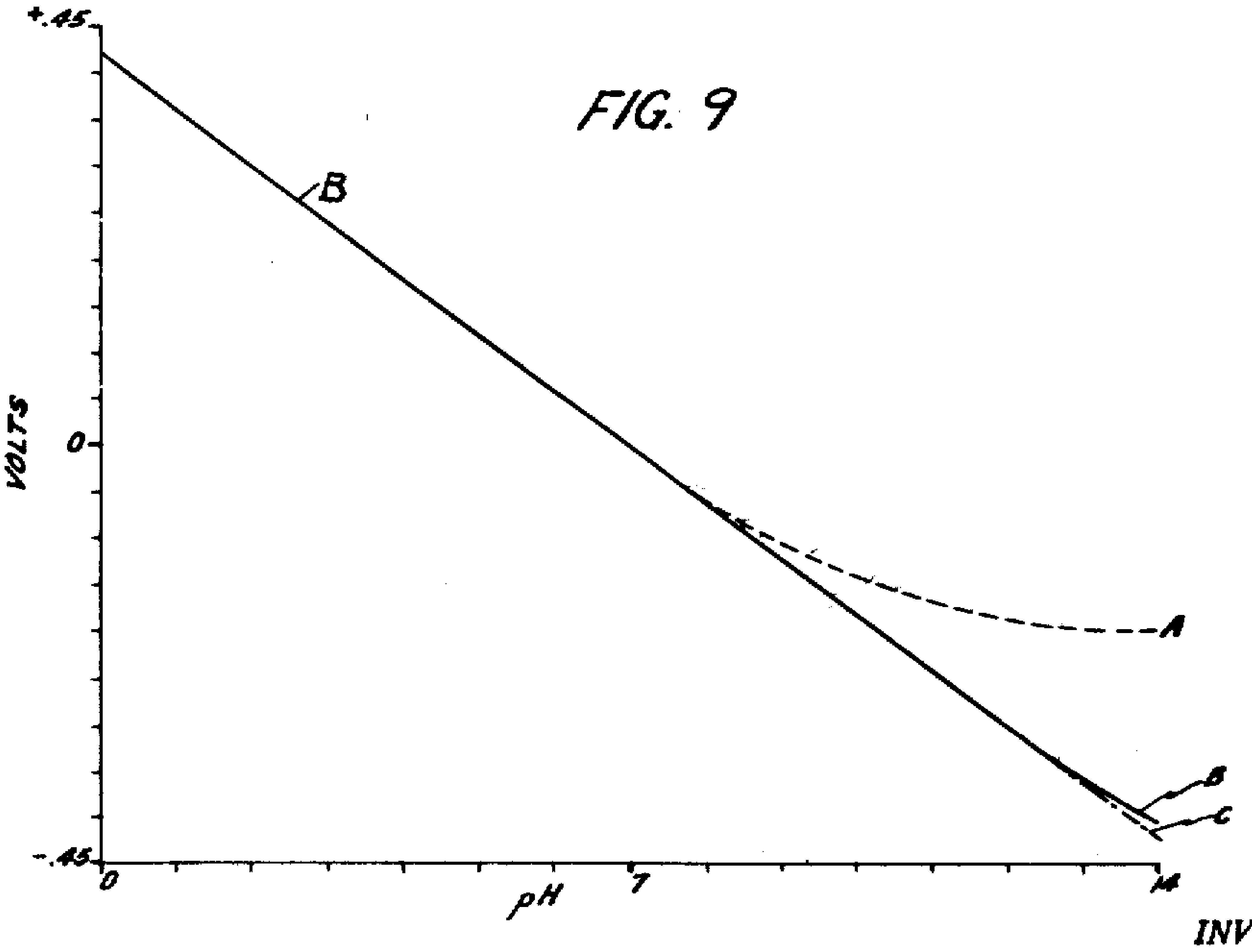

FIG. 9

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July 6, 1948. G. A. PERLEY 2,444,845

PH-RESPONSIVE GLASS ELECTRODE

Filed May 9, 1946 7 Sheets-Sheet 5

TABLE 5

FIG. 5 INFLUENCE OF La_2O_3 (OXYGEN MODIFIER) AND SiO_2 CONTENT ON GLASS STABILITY.

No.	MOL PER CENT						AVERAGE MEGOHMS AT 25°C	pH ERROR, 25°C, 2 N SODIUM 12.8 TO 13.0 pH	
	R_2O		MO		OM	XO_2			
	Li	Cs	Ca	Ba	La_2O_3	Si		DAYS 2	MONTHS 6
NY	25	0	0	8	0	67	500	0.25	0.66
MZ	25	1	0	9	0	65	750	0.32	2.05
NJ	25	2	0	10	0	63	1300	0.90	2.66
ML	26	2	3	5	0	64	700	0.10	3.00
NP	25	3	0	7	0	65	300	0.63	2.60
MT	25	0	0	7	3	65	800	0.15	0.15
NK	25	2	0	8	2	63	2000	0.08	0.07
MH	25	1	0	7	2	65	1700	0.17	0.16
NA	25	1	0	4	5	65	670	0.15	0.18
MK	25	0	0	5	4	66	460	0.30	0.40
MO	26	2	4	4	1	63	1300	0.10	0.07
NV	28	2	0	5	2	63	80	0.12	0.07

TABLE 5A

FIG. 5A CONTINUOUS OPERATION IN CITY WATER AT 90-92°C

No.	MOL PER CENT						AVERAGE MEGOHMS AT 25°C	pH ERROR, 25°C, 2 N SODIUM 12.8 TO 13.0 pH		
	R_2O		MO		OM	XO_2				
	Li	Cs	Ca	Ba	La_2O_3	Si		DAYS 2	WEEK 1	WEEKS 6
JR	24	2	3	3	0	68	800	0.39	1.60	2.20
JT	24	1	3	5	0	67	600	0.50	1.13	1.65
LD	25	2	2	3	1	67	500	0.43	1.40	1.70
NB	25	2	2	5	3	63	1600	0.30	0.12	0.05
NK	25	2	0	8	2	63	2000	0.25	0.16	0.10
NY	25	0	0	8	0	67	480	0.86	4.85	–

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July 6, 1948. G. A. PERLEY **2,444,845**

PH-RESPONSIVE GLASS ELECTRODE

Filed May 9, 1946 7 Sheets-Sheet 6

TABLE 6

FIG. 6 INFLUENCE OF THE PRESENCE OF OXYGEN MODIFIERS

MOL PER CENT COMPOSITION} $26Li_2O-2Cs_2O-2CaO-4BaO-2OM-64SiO_2$

No.	OXYGEN MODIFIER	AVERAGE MEGOHMS AT 25°C	pH ERROR, 25°C, 2 N SODIUM 12.8 TO 13.0 pH	
			DAYS 2	MONTHS 6
OG	La_2O_3	450	0.07	0.07
OI	Pr_2O_3	450	0.07	0.10
OJ	Nd_2O_3	450	0.08	0.15
OK	CeO_2	480	0.10	0.16
PX	TeO_3	380	0.17	0.17
OS	P_2O_5	150	0.32	0.21
OH	Co_2O_3	2400	0.28	0.30
ON	ZrO_2	250	0.20	0.33
OM	TiO_2	280	0.10	0.35
PU	Cb_2O_5	210	0.16	0.35
OQ	Ta_2O_5	200	0.12	0.40
OP	ThO_2	280	0.12	0.40
OU	As_2O_5	190	0.40	0.46
OO	UO_2	300	0.25	0.47
OT	B_2O_3	360	0.22	0.50
PM	Cr_2O_3	200	0.17	0.50
OW	WO_3	380	0.17	0.54
OZ	CoO	420	0.25	0.54
PW	SeO_2	200	0.23	0.78 (3 Mos.)
OR	V_2O_5	200	0.58	1.06
OL	Al_2O_3	290	0.25	1.10
OX	MoO_3	150	0.31	1.10
PV	Tl_2O_3	720	0.60	2.83 (4 Mos.)

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July 6, 1948. G. A. PERLEY **2,444,845**

PH-RESPONSIVE GLASS ELECTRODE

Filed May 9, 1946 7 Sheets-Sheet 7

TABLE 7

FIG. 7

INFLUENCE OF LANTHANUM OXIDE-SILICA RATIO ON SODIUM ERROR

NO.	MOL PER CENT						AVERAGE MEGOHMS AT 25°C	pH ERROR, 25°C, 2 N SODIUM 12.8 TO 13.0 pH.	
	R_2O		MO		OM	XO_2			
	Li	Cs	Ca	Ba	La_2O_3	Si		DAYS 2	MONTHS 6
LD	25	2	2	3	1	67	500	0.12	0.16
OF	25	2	2	4	1	66	450	0.20	0.20
OE	25	2	2	4	3	64	1000	0.13	0.08
MW	25	2	2	4	4	63	1800	0.10	0.06
NY	25	0	0	8	0	67	500	0.25	0.66
LS	25	1	0	7	0	67	200	0.14	0.43
MH	25	1	0	7	2	65	1600	0.10	0.31
NI	25	1	0	7	6	61	2800	0.10	0.08

TABLE 8

FIG. 8

INFLUENCE OF THE MO TYPE OF CONSTITUENT ON GLASS

No.	MOL PER CENT							AVERAGE MEGOHMS AT 25°C	pH ERROR, 25°C, 2 N SODIUM 12.8 TO 13.0 pH	
	R_2O		MO			OM	XO_2			
	Li	Cs	Ca	Sr	Ba	La_2O_3	Si		DAYS 2	MONTHS 6
NK	25	2	0	0	8	2	63	2400	0.08	0.07
NS	25	2	2	0	6	2	63	1500	0.09	0.10
NT	25	2	4	0	4	2	63	1350	0.10	0.05
NU	25	2	6	0	2	2	63	1300	0.10	0.08
NW	25	2	8	0	0	2	63	1200	0.09	0.10
NX	25	2	2	5	0	2	64	1500	0.09	0.12
NB	25	2	2	0	5	3	63	1600	0.12	0.10
OY	26	2	4	0	2	2	64	500	0.09	0.15
OG	26	2	2	0	4	2	64	450	0.07	0.07
PR	28	1	5	0	0	3	63	300	0.20	0.28
PS	28	1	0	5	0	3	63	170	0.19	0.15
PP	28	1	0	0	5	3	63	200	0.09	0.10
NV	28	2	0	0	5	2	63	80	0.12	0.07

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UNITED STATES PATENT OFFICE

2,444,845

pH-RESPONSIVE GLASS ELECTRODE

George A. Perley, Wyncote, Pa., assignor to Leeds and Northrup Company, Philadelphia, Pa., a corporation of Pennsylvania

Application May 9, 1946, Serial No. 668,392

8 Claims. (Cl. 204—195)

My invention relates to pH-responsive glass electrodes, utilizable for example in determination of the pH, representative of the magnitudes of concentration of hydrogen-ions or hydroxyl-ions and of acidity and alkalinity; more particularly my invention relates to the compositions, for the membranes of aforesaid electrodes, of the characteristics disclosed in my original application Serial No. 467,069, filed November 26, 1942 (now abandoned), of which this application is in part a continuation, and of the charatceristics hereinafter disclosed.

In general, glass electrodes of compositions known and used prior to my invention have been subject to large "sodium error" whose magnitude was dependent upon the temperature and the pH of the solution, and upon the effect on the electrode glass by the sodium content of that solution, commonly known as the test solution; none of the aforesaid prior electrodes was suited for measurement of pH over long periods of time because of occurrence of changes in calibration, and impairment of speed of electrode response to changes in pH of the test solution; their sodium error, in terms of error in the pH measured by them, was great; none was suited for measurements of pH throughout the entire or substantially entire range from 0 pH to 14 pH; in general they were unsuitable for measurement of pH of solutions of alkalinity greater than about 9.6 pH; and none of them was suitable for continuous measurement of pH of solutions whose temperatures substantially exceeded 50° C.

In accordance with my invention operative and practical qualities of glass electrodes have been greatly improved: in respect to reduction of sodium error, from greater than 1 pH to about .5 pH and as low as .25 pH to about .10 pH, while still exhibiting very high qualities in respect to electrical volume-resistance of the glass membrane of the electrode; in respect to high stability or permanence in qualities and behavior over long periods of continuous use; in respect to measurement of pH of solutions having temperatures ranging from 0° C. to about 100° C.; in respect to procurement of consistently reproducible voltage/pH (potential/pH) characteristic which is rectilinear throughout substantially the entire range of pH measurements, from 0 to 14 pH, with a slope represented, for example, by about 60 millivolts per one pH; and in respect to desirable aspects and qualities herein more particularly referred to.

More particularly, my invention is characterized by inclusion in the glass membrane compo-

sitions, in addition to the usual components $R_2O—MO—XO_2$, of an oxygen modifier, OM, (one or more of the numerous oxides, including the rare earth metal oxides, hereinafter referred to) having the effect of increasing the ratio of oxygen to silicon in the glass, so securing or maintaining high the magnitude of that ratio when the mol per cent of SiO_2 is low, e. g., 59 to 66 per cent, thereby reducing sodium error and in addition greatly increasing stability and permanence of behavior of the electrode for long periods of time at normal and elevated temperatures. An outstanding example of oxygen modifier is one of the rare earth metal oxides, lanthanum oxide, La_2O_3. The oxygen modifier may be the oxide or a mixture of oxides of one or more of the hereinafter specified metals or elements, including rare earth metals. The mol percentage of oxygen modifier is in general small, for example from about 0.5 to about 6 mol per cent of the entire composition, as compared with the relatively greater mol per cent of the associated XO_2 component, such as SiO_2 which preferably constitutes the relatively low proportion of from about 59 to about 66 mol per cent of the entire glass composition; the mol percentages of the oxygen modifier and of the associated SiO_2 are complemental, in the sense that when the mol percentage of one is changed, within the approximate limits aforesaid, the mol percentage of the other, within its approximate limits aforesaid, changes in opposite sense and by approximately equal amounts.

My invention consists of a pH-responsive electrode of silicate glass yielding marked practical improvements and whose composition is represented by a prefusion mixture of silica with alkali metal oxides and alkaline earth metal oxides, and having in conjunction therewith, to provide high ratio of oxygen to silicon, one or more of the oxides hereinafter for brevity designated as oxygen modifiers.

My invention resides in the glass electrodes and compositions therefor hereinafter described and claimed.

For examples of my compositions and their characteristics, and for tables illustrative of various aspects and characteristics of my invention, reference is had to the accompanying drawings, in which:

Fig. 1, Table 1, affords numerous examples, including some from aforesaid original application, of results of extensive research respecting compositions and their operative properties of electrical volumetric-resistances and sodium errors in magnitudes of pH, after periods of use for various lengths of time;

Fig. 2, Table 2, is illustrative of effects of compositions upon aforesaid electrical resistance of the glass electrode;

Fig. 3, Table 3, is illustrative of the adverse effects of some of the components of glass compositions upon the magnitude of the sodium error of the resultant glass electrodes;

Fig. 4, Table 4, is illustrative of the influence or effect of cesium on the sodium error;

Fig. 5, Table 5, is illustrative of the effect of the oxygen modifier and SiO_2 content on the stability of the electrode glass;

Fig. 5A, Table 5A, illustrates behavior of various glass electrodes in continuous operation at elevated temperature;

Fig. 6, Table 6, is illustrative of the influence of the presence, in certain of my glass compositions, of various oxygen modifiers;

Fig. 7, Table 7, is illustrative of the influence, on the sodium error, of the proportion of lanthanum oxide to silica ratio;

Fig. 8, Table 8, is illustrative of the influence on the electrode glass of the MO type of component; and

Fig. 9 is a graph illustrating the voltage/pH characteristic of my glass compositions.

My glass compositions are the result of need to discover, as between components of different characters, or between individual oxides and their mol percentages or proportions, which shall well or best attain as many as possible, and to the greatest extent of each possible, of desirable aspects or characteristics as follows:

(*a*) The glass electrode should yield a rectilinear voltage/pH characteristic at least closely approximating that afforded by the ideal or perfect hydrogen gas electrode; thus for every change of one pH of the test solution, at 25° C., the potential of the glass electrode should change 0.05912 volt. Actually a change of 0.003 volt for a change of 0.05 pH (60 millivolts per one pH) is fairly representative.

(*b*) The glass electrode should produce the same H-ion to electro-motive-force relationship for both presence and absence of metallic ions in and from the test solution; thus the presence in the test solution of sodium, potassium, etc., ions, not permissible with glass electrodes known before my invention, should have no influence upon the electro-motive-force/pH relationship.

(*c*) The glass of the electrode should have a long-time stability at temperatures of the range 0° C. to nearly 100° C.; which is to say, the composition of the glass should not be altered or affected by the usual test solutions in which it may be immersed, for pH measurement, even at elevated temperatures.

(*d*) The glass of the electrode should be of easily workable quality, to yield a glass membrane or membranous bulb of relatively robust characteristics, safely to withstand ordinary handling and use. The electrode composition should not be of character subject to devitrification or opacity which connotes lack of essential homogeneity.

(*e*) The electrical volume-resistance of the composition for the glass membrane should be low, because the greater the resistance, the greater the problems of IR drop, leakage, pick-up and various other types of electrical disturbances. A bulb or membrane of the dimensions herein by way of example stated, having a volume-resistance substantially in excess of 800 megohms at any operating temperature, generally is deemed undesirable. In this connection it is recalled that such an electrode having at 0° C. a volume-resistance of 800 megohms, at 25° C. has a resistance of 45 megohms, and at 50° C. has a resistance of only 4 megohms. Similarly a glass electrode bulb or membrane having at 25° C. a volume-resistance of 500 megohms has, at 50 C., a resistance of 45 megohms, and at 90° C., a resistance of 2 megohms.

(*f*) Of great practical importance is the need, for practical and commercial use, that the glass electrode continuously for long periods of use shall have sodium error of low magnitude. The sodium error, contemplated also by (*c*) above, is conveniently expressible in terms of the amount of error in pH caused by the sodium content of the test solution. In the tables, aforesaid Figs. 1–8, sodium errors are expressed in terms of magnitudes of pH error at 25° C. for 2N sodium and at 12.8 to 13.0 pH.

Although the glasses or glass compositions here of interest comprise complex silicates of certain metals, or homogeneous mixtures of silicates of those metals with silica, their composition is in each case expressed in terms of oxides, and, to use my conventional notation, each composition is represented by an aforesaid general formula $R_2O/OM/MO/XO_2$ in which, for purposes of in my terms defining my invention:

R is one or more of the metals lithium (Li), cesium (Cs), rubidium (Rb), potassium (K), and sodium (Na);

M is one or more of the metals calcium (Ca), strontium (Sr), barium (Ba), and magnesium (Mg);

X, except as to small quantities of contaminants unavoidably present, is silicon (Si);

OM is one or more of the oxygen modifiers, consisting of the oxides and rare earth metal oxides herein referred to and producing the herein described beneficial effects accruing from increase in the ratio of oxygen to silicon.

In addition to aforesaid components

$$R_2O—MO—XO_2$$

there preferably is used one or more of aforesaid oxygen modifiers, which for present purposes may be generically designated as component OM, in which, for purposes of defining my invention, there may be employed:

One or more of the oxides, not easily attacked by alkaline solutions of sodium, potassium, or the like, of the following metals or elements, zirconium, ZrO_2; titanium, TiO_2; tellurium, TeO_2; phosphorus, P_2O_5; columbium, Cb_2O_5; tantalum, Ta_2O_5; thorium, ThO_2; arsenic, As_2O_5; uranium, UO_2; and of one or more of the rare earth metals cerium, CeO_2; yttrium, Y_2O_3; lanthanum, La_2O_3; praseodymium, Pr_2O_3; neodymium, Nd_2O_3; samarium, Sm_2O_3; and the like oxides of the further rare earth metals europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium.

Substantially to eliminate the sodium error in the measurement of pH, the composition of the glass of the electrode should not be such that any of its constituents is to appreciable extent exchangeable with sodium ions of the test solution; the silicon and oxygen of the silicates should be so chemically bound that there are not present to substantial extent unsatisfied valences productive at the surface of the glass of sodium silicate by reaction of sodium ions of the test solution, in which the electrode glass is immersed, with one or more constituents of the glass. This end may be accomplished by selection of ratios between R_2O, MO, and especially OM, and XO_2 based on the considerations hereinafter discussed.

For best chemical stability of the R_2O component, I have found cesium may be used. In order to produce a glass whose electrical volume-resistivity is not excessively high at least a substantial or preponderant part of the R_2O component should comprise lithium. Use of lithium as the sole metal of the R_2O component is satisfactory when it constitutes, in terms of molecular percentage of the composition, not more than about 30%, to avoid undue decrease in durability or useful life of the electrode. The R_2O component of my preferred glasses comprises both lithium and cesium in percentages herein indicated.

Rubidium may be used instead of cesium with about equal performance and with substantially similar limitations upon selection of its proportions with respect to other constituents of the glass.

Within narrow percentage limits, cesium may be replaced by potassium with retention of low sodium error characteristic; in general, increasing the K_2O content of the R_2O component of the glass effects relatively great increase in the electrical volume-resistivity while decreasing it results in impairment of stability of the glass in highly alkaline solutions.

In general, the limits for the oxides of cesium, rubidium, potassium or sodium are from 0 to about 3 mol per cent of the total of the constituents; and of lithium from about 17 to 32 mol per cent.

The MO component may comprise CaO in combination with MgO (glass IA). Such glasses draw easily and are easily blown into clear thin membranous bulbs.

In the glasses (NB, MO and MW) found best suited for applications requiring long continued exposure of the electrode to the test solution at elevated temperature, the MO component of the glass preferably comprises both calcium and barium oxides.

Strontium oxide may be substituted for barium oxide with some effect upon the electrical volume-resistance, but even less effect upon other properties, such as low sodium error, stability, and rapidity of response.

Concerning the selection and proportions of the XO_2 component of glasses of my invention, it is entirely SiO_2.

In all cases, the molecular percentage of the XO_2 component should lie within the range of from about 59 to about 66% of the total composition of the glass; or from about 63 to about 65 mol per cent for my preferred glasses exemplified by the types following:

Li_2O—Cs_2O—BaO—La_2O_3—SiO_2, such as glass NV
Li_2O—Cs_2O—BaO—CaO—La_2O_3—SiO_2, such as glass NB
Li_2O—BaO—La_2O_3—SiO_2, such as glass MT
Li_2O—Cs_2O—SrO—CaO—La_2O_3—SiO_2, such as glass LB

Referring to Fig. 1: Table 1 comprises numerous compositions comprehended by my invention, and illustrations of influences by different kinds of, and variations of proportions of, individual constituents or combinations thereof. The first 13 compositions, GR to IC, are examples of those disclosed in my aforesaid original application.

The compositions of Table 1 include those whose stability during continuous use as pH measuring electrodes for long periods, including periods from about six months to about two years, has been exceptionally good.

Of the compositions of Table 1 not disclosed in aforesaid original application, 66 are characterized by the significant content of SiO_2, to wit, less than 66 mol per cent, in conjunction with various oxygen modifiers; and 58 of the compositions not disclosed in aforesaid original application, are characterized by various contents of Cs_2O.

Aforesaid 13 compositions of my original application, are characterized in all but one case by SiO_2 content less than 66 mol per cent; each of 6 of aforesaid 13 compositions includes an oxygen modifier; and each of 11 of aforesaid 13 compositions includes cesium.

In Table 1, all of the oxygen modifiers are La_2O_3, except as therein otherwise indicated.

The electrical volume-resistance of a pH responsive glass, in other respects suitable or practical for commercial or laboratory use, may pose a serious problem; the final choice of a glass composition is dependent upon or influenced in part by aforesaid resistance of the glass membrane or membranous bulb whose thickness may not, for purposes of reducing its aforesaid volumetric-resistance, be reduced below that magnitude which shall assure the membrane shall be sufficiently robust to withstand ordinary handling and use, particularly when the glass electrode as usual contains a solution.

A pH-responsive glass of low electrical volume-resistance—Table 2, Fig. 2, preferably less than 80 megohms at 25° C.—is of advantage in that it is subject to less voltage error due to electrical leakage, as along the external surface of the stem of the glass electrode, adversely affecting the pH measurements; low resistance is also conducive to lessening of IR drop errors due to too high grid current of an electronic device for measuring the voltage developed by the pH measuring cell comprising the test solution, the measuring electrode of pH-responsive glass and the usual reference electrode; low electrical resistance is conducive also to less error due to electrostatic pick-up or electrical disturbances ambient to the glass electrode or the pH measuring cell.

A high SiO_2 content (e. g., approximately 66 to 70 mol per cent) tends to procurement of low electrode resistance; but such high SiO_2 content results in undesirably high or prohibitive sodium error. A high Li_2O content (e. g., about 29 mol per cent or more) contributes to low electrode resistance; but such Li_2O content also results in undesirable or prohibitive magnitude of sodium error. The presence in the composition of a BaO constitutent results in higher electrical resistance than does CaO.

The choice of composition, with special regard to the electrical volume-resistance of the glass, is well illustrated by glasses NB and NV, Tables 1 and 2; thus, other things being the same, the NV glass is preferable to that of the NB type, though the sodium errors of both at room temperatures are substantially the same; but for use with solutions of elevated temperatures, the resistance of glass NB, though high at ordinary temperatures, is, at elevated temperatures, suitably low.

Referring to Fig. 3, Table 3: In general, the Na_2O type of glass (such as PB, MA) has a lower resistance than an Li_2O type (such as PA, LZ) which in turn is of lower electrical volume-resistance than a K_2O type (such as PC, MB). In general, however, the sodium errors of Na_2O types are high.

Choice between Li_2O, and Na_2O, K_2O, Rb_2O or Cs_2O types of compositions is simplified in part by the fact it is difficult to procure a high (about 26 mol per cent) Rb_2O or Cs_2O content, because of the high rates at which the oxide-producing salts of the two elements Rb and Cs decompose at the temperature of the glass-making furnace. Rb_2O and Cs_2O readily decompose even at low temperature such as about 600° C., and the more rapidly at higher temperatures. The temperature range for fusion of my mixtures of oxide yielding salts varies from about 1100° C. to about 1300° C.

The use of Li_2O in combination with CaO and high SiO_2 has been suggested (Zeitschrift fur Physikalische Chemie, A-160, p. 366, 1932; S. I. Ssokolof and O. H. Passynsky); I have found their glass is difficult to manufacture.

The sodium error of a Li_2O type of composition, consisting of a favorable mixture or combination with Li_2O of BaO with La_2O_3 and SiO_2, or Li_2O with BaO, CaO, La_2O_3 and SiO_2, is far lower than for the generally corresponding Na_2O or K_2O types of composition. Although the electrical resistance aforesaid of an equivalent Na_2O type of composition is lower than that for the Li_2O type, it is distinctly more advantageous or in some cases necessary to employ Li_2O in proper here disclosed proportions in order to secure freedom from large or prohibitive sodium error, i. e., to secure my new low order of sodium error.

Table 3 illustrates the relative merits of the Li_2O, the Na_2O and the K_2O types of glasses. It is predictable and observable from Table 3 that a Li_2O type of composition will have a smaller sodium error than a Na_2O type of composition, which in turn will have a smaller sodium error than a K_2O type of glass. Respecting attack upon the electrode membrane by sodium salts in the solutions whose pH is under measurement, those salts will not materially alter my Li_2O—SiO_2 compositions, whereas sodium salts in the test solutions will greatly change or affect a corresponding K_2O—SiO_2 composition with resultant prohibitively high sodium error.

Referring to Fig. 4: Table 4 shows the presence of even small amounts (about 1 to about 2 mol per cent) of Cs_2O as a constituent of the glass electrode composition highly significantly reduces the sodium error, irrespective of whether the MO component of the glass comprises any one or more of the BeO, MgO compositions with either CaO or SrO in place of BaO.

While the influence of Cs_2O (or Rb_2O) in my compositions may appear small because present in numerically small percentage, its effect is in fact relatively great in reducing sodium error, herein always tabulated in terms of pH error.

Nevertheless my broadly preferable Li_2O—Cs_2O—BaO—La_2O_3—SiO_2 type of glasses are important even should aforesaid small additions of Cs_2O be reduced in magnitude or entirely omitted because of the presence of La_2O_3 or equivalent oxygen modifier.

Referring to Fig. 5, Table 5: A highly important result of my research is the discovery of the importance of the use of a relatively low SiO_2 content, to wit, of about 59 to about 66 mol per cent (which per se is in general significantly lower than suggested or used for glass electrodes prior to my invention, for example 71 to 74 mol per cent) in combination with an oxygen modifier (which is my term for brief designation of the numerous oxides, of my class thereof including such as La_2O_3, having the herein described beneficial effects) which is not easily attacked by either acid or alkaline test solutions of from about 0 pH to about 14 pH. The oxygen modifier chosen should be of character not easily combining with the SiO_2 component thereby to form an undesirable stable compound. The effect and purpose of addition of an oxygen modifier is to supply oxygen to and for the glass network structure, thereby securing high ratio of oxygen to silicon, which is novel, in effecting both significant reduction of sodium error (due to low proportion of SiO_2) and significant increase in the stability, permanence of behavior, of the electrode for significantly longer periods of use at normal and particularly (Fig. 5A) at elevated temperatures.

Fig. 6: Table 6 is illustrative of alternatives for the particular oxygen modifier La_2O_3. In this table glass OH is included for contrast, because it is not itself recommended because of its high volume-resistance and its unworkability. The oxygen modifiers of glasses OW to PV, foot of Table 6, are included for contrast and general guidance; they are among those of low orders of suitability or practicability as compared with my more preferable compositions also having oxygen modifier components.

Referring to Fig. 7: Table 7 illustrates the influence, on sodium error, of the ratio of the La_2O_3 content to the content of SiO_2.

This table shows, as by glasses OF, OE and MW, that with the Li_2O—Cs_2O—CaO—BaO content held constant, or with the Li_2O—Cs_2O content (glasses MH and NI) held constant, the decrease in mol per cent of SiO_2 with a corresponding per cent increase in the oxygen modifier, such as La_2O_3, produces a glass having significantly low sodium error.

Referring to Fig. 8: In Table 8 it is shown that, provided the Li_2O content does not exceed 25 mol per cent, it is a matter of indifference so far as concerns sodium error whether the MO component be calcium, strontium or barium, or mixtures of two or more thereof, so long as there be present an oxygen modifier, La_2O_3 or equivalent, and so long as the SiO_2 content is below, or does not materially exceed, 66 mol per cent, even with La_2O_3 or other oxygen modifier present, the sodium error is practically unaffected by choice of the MO component. However with higher Li_2O content, for example about 28 mol per cent, the use of BaO or SrO is preferred over CaO.

In Fig. 9 is illustrated the voltage/pH characteristic, B, of my hereinbefore described glass electrode compositions, for solutions of 2N sodium. The cell employed comprised, besides the glass electrode and the test solution, a reference electrode in a 7 pH solution. It will be noted the characteristic B is rectilinear throughout the range from about 0 to 14 pH; and has a slope, like that of the ideal, C, or perfect hydrogen pH measuring electrode, corresponding with about 60 millivolts per one pH.

The voltage/pH characteristic of glass electrodes known and used prior to my invention is substantially coincident with the aforesaid characteristic B from about 0 pH to slightly above 8 pH, from which latter point onward, to about 14 pH, it is a branch A from characteristic B, and above 12 pH is substantially parallel to the axis of abscissae.

From the foregoing, it will be noted:

That a fundamental, in some aspects the most important fundamental of my glass electrodes and compositions therefor, is that the SiO_2 content shall be less than 66 mol per cent, and should have associated therewith a network oxygen modifier;

That the oxygen modifiers, singly or in mixture, such as the rare earth oxides La_2O_3, Pr_2O_3, Nd_2O_3, CeO_2, etc., and the oxides P_2O_5, TeO_3, ZrO_2, TiO_2, ThO_2, Ta_2O_5, Cb_2O_5, As_2O_5 give substantially equally good results. In contrast with the foregoing, oxides WO_3, B_2O_3, Al_2O_3, UO_2, Co_2O_3, and V_2O_5 yield effects similar in kind, but are less desirable. In general, oxide modifiers which are attacked by alkaline test solutions are not desirable;

That Li_2O, as R_2O component, is highly important to low sodium error. However, addition of Cs_2O or Rb_2O to the Li_2O results in favorable substantial further decrease of the sodium error. Na_2O and K_2O are in general undesirable in respect to low sodium error;

That use of CaO, SrO and BaO for one or more constituents of the MO component, is helpful when dealing with from about 22 to about 28 mol per cent Li_2O. However, there is little choice, from the standpoint of their sodium error characteristics, whether SrO or BaO be used alone or in combination with the other sodium-error-reducing oxides, to wit, Li_2O—Cs_2O—La_2O_3—SiO_2. Use of BeO and/or MgO is not desirable when low sodium error is in point;

That outstanding characteristics of those of my glass compositions comprising from about 59 to about 66 mol percent SiO_2, plus about 6 to about 0.5 mol per cent of oxygen modifier, reside not only in their low sodium error, but also in their outstanding performance when used in test solutions at high temperatures, as exemplified by stability or constancy of high performance in continuous operation for long periods in flowing water even at 90° C.;

And that with respect to my compositions including oxygen modifiers, the R_2O component should constitute from about 22 to about 30 mol per cent of the entire composition; the OM component from about 6 to about 0.5 mol per cent of oxygen modifier; the XO_2 component should comprise from about 59 to about 66 mol percent, and the sum of the mol percentages of the OM and XO_2 components should be about 70 mol per cent of the entire composition, the remainder of the composition consisting of the component MO.

In manufacture of my glasses carbonates, nitrates, or other salts or compounds of the R metals, the OM metals and of the M metals are mixed with a suitable type of sand, such as potters sand or high grade quartz sand, to provide the XO_2 component, and the mixture fused in a crucible of platinum to avoid contamination of the melt by impurities usually or frequently present in refractory crucibles. The proportions by weight of the various ingredients are chosen to afford the above specified molecular percentages of oxides of the R metal, M metal, the OM metal and silicon. The mol percentages, for practical purposes of composing the mixtures for fusion, may be taken as the same as the desired mol percentages existing after fusion.

During aforesaid heating process, requiring temperatures of about 1700° F. to 2400° F., the carbonates or other salts or compounds are decomposed, carbon dioxide is evolved, and interaction of the resultant oxides with the sand occurs.

In working the molten glass, it is subjected to a considerably lower temperature, about 1200° to 1300° F., lower than its melting temperature, depending upon the particular glass. In forming the glass into a pH responsive member, as by blowing it into bulb form, the flame temperature should be maintained as low as possible and the oxygen content of the flame should not be allowed to become too high; otherwise there may be abnormal loss of lithium or other element of the glass with resultant impairment of its value for pH measurements.

Membranes which are not clear, due to devitrification or other cause, should be discarded as usually unsuited for use in pH measurements.

The completed electrode may be in the general shape of a test tube all whose glass is of the same composition; or the electrode may be a bulb blown from one of the glasses above described upon a tubular stem of glass of different composition. To distinguish between my glass electrodes having different fields of use or different characteristics, there may be used stems of differently colored glasses, each identifying a particular glass bulb or membrane composition.

The stem must have low surface conductivity (low electrical leakage) and high volumetric (electrical) resistance to avoid secondary errors of measurement. In addition, the glass of the stem must have about the same thermal coefficient of expansion as that of the glass to which attached and, of great importance, the glass of the stem must not appreciably diffuse into the glass of the electrode proper when joined. By way of example, the glasses known as Corning #001 or 01 lead glass are suitable for the stems; on the other hand some glasses, including soda lime glass, have been unsuitable because they diffused into the electrode glass and gave rise to appreciably large sodium errors when the electrode assembly was used for measurements in strongly alkaline test solutions.

The magnitudes of resistance listed in the tables are for bulbs of approximately 8 to 9 mm. outside diameter, about .2 mm. thick, weight of bulb about .15 gram, joined to a stem of approximately 10 mm. internal diameter. The volume-resistances were obtained in each case by measurement of the resistance between conductors in solutions respectively disposed on opposite sides of and engaging all of the membrane of the glass electrode. The resistances of the membranes at 90° C. are approximately five thousandths of the resistances at 25° C.

The herein indicated sodium errors, in terms of error in pH, were measured under conditions of 2N sodium solution of 12.8 to 13.0 pH, at 25° C.

The mol percentages herein specified are in each case those of an entire glass composition.

As exemplary of measuring systems with which the glass electrodes comprehended by my invention may be used to advantage, reference is made to United States Letters Patent Nos. 2,108,294, Doyle et al.; 2,285,482, Wunsch; and 2,367,746, Albert J. Williams, Jr.

What I claim is:

1. A pH-responsive glass electrode of composition having from about 20 to about 30 mol per cent Li_2O, from about 0.5 to about 6 mol per cent

La_2O_3, from about 59 to about 66 mol per cent SiO_2, and the remainder consisting of one or more of the oxides CaO, SrO and BaO.

2. A pH-responsive glass electrode of composition having about 28 mol per cent Li_2O, about 2 mol per cent Cs_2O, about 5 mol per cent BaO, about 63 mol percent SiO_2, and about 2 mol per cent La_2O_3.

3. A pH-responsive glass electrode of composition having about 25 mol per cent Li_2O, about 2 mol per cent Cs_2O, about 2 mol per cent CaO, about 5 mol per cent BaO, about 63 mol per cent SiO_2, and about 3 mol per cent La_2O_3.

4. A pH-responsive glass electrode of composition having from about 20 to about 30 mol per cent Li_2O, 0 to about 3 mol percent Cs_2O, about 59 to about 66 mol per cent SiO_2, about 6 to about 0.5 mol per cent La_2O_3, and the remainder consisting of the oxide SrO.

5. A glass electrode having a sodium error not exceeding 1 pH at 2N sodium at 12.6 pH at temperature 25° C. to 35° C. whose voltage/pH characteristic is reproducible throughout the range 0 pH to 14 pH, and whose glass network structure is represented by the prefusion mixture consisting of silica with Li_2O and at least one of the oxides of the group consisting of CsO, Rb_2O, Na_2O, K_2O, and with at least one of the oxides of the group consisting of CaO, BaO, SrO, and high ratio of oxygen to silicon in said structure provided by inclusion in aforesaid mixture of at least one of the oxides of the group consisting of TeO_3, P_2O_5, TiO_2, ZrO_2, As_2O_5, Cb_2O_5, Ta_2O_5, ThO_2, B_2O_3 and the rare earth metal oxides.

6. A glass electrode having a sodium error not exceeding 1 pH at 2N sodium at 12.6 pH at temperature 25° C. to 35° C., whose voltage/pH characteristics is reproducible throughout the range 0 pH to 14 pH, and of composition consisting of, in mol percentages of the entire glass composition, from about 22 to about 28 per cent Li_2O with not exceeding about 3 percent additional of at least one of the oxides of the group consisting of Na_2O, Cs_2O; Rb_2O and K_2O, at least one of the oxides of the group consisting of BaO, CaO, SrO totalling not more than from about 3 percent to about 9 percent, and silica from about 59 to about 66 percent with from about .5 percent to about 6 percent of at least one oxygen modifier of the group consisting of TeO_3, P_2O_5, TiO_2, ZrO_2, As_2O_5, Cb_2O_5, Ta_2O_5, ThO_2, B_2O_3 and the rare earth metal oxides.

7. A glass electrode having a sodium error not exceeding 1 pH at 2N sodium at 12.6 pH at temperature 25° C. to 35° C., whose voltage/pH characteristic is reproducible throughout the range of 0 pH to 14 pH, and whose composition in mol percentages consists of Li_2O aggregating with at least one of the oxides of the group consisting of Cs_2O, Rb_2O, Na_2O, K_2O from about 25 percent to about 31 percent, from about 3 percent to about 9 percent of at least one of the oxides of the group consisting of BaO, CaO, SrO, a component of not more than about 6 percent of at least one of the oxygen modifiers of the group consisting of TeO_3, P_2O_5, TiO_2, ZrO_2, As_2O_5, Cb_2O_5, Ta_2O_5, ThO_2, B_2O_3 and the rare earth metal oxides, and a component of silica not exceeding about 66 per cent.

8. A pH-responsive electrode of glass having a sodium error not exceeding 1 pH at 2N sodium at 12.6 pH at temperature 25° C. to 35° C., whose voltage/pH characteristic is reproducible throughout the range 0 pH to 14 pH, and whose composition is represented by a prefusion mixture consisting af silica, lithia, at least one alkaline earth metal oxide, and at least one of the oxygen modifiers of the group consisting of TeO_3, P_2O_5, TiO_2, ZrO_2, As_2O_5, Cb_2O_3,Ta_2O_5, ThO_2, B_2O_3 and the rare earth metal oxides.

GEORGE A. PERLEY.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,311,977	Coleman	Feb. 23, 1943

OTHER REFERENCES

"Glass Electrode," by Dole (1941), pages 69, 74, 75, 89, 90.

"Journal of Biological Chemistry," volume 81 (1929), page 582; article by Mirsky et al.

Certificate of Correction

Patent No. 2,444,845. July 6, 1948.

GEORGE A. PERLEY

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Column 11, line 27, claim 5, for "CsO" read *Cs_2O*; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 16th day of November, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.

La_2O_3, from about 59 to about 66 mol per cent SiO_2, and the remainder consisting of one or more of the oxides CaO, SrO and BaO.

2. A pH-responsive glass electrode of composition having about 28 mol per cent Li_2O, about 2 mol per cent Cs_2O, about 5 mol per cent BaO, about 63 mol percent SiO_2, and about 2 mol per cent La_2O_3.

3. A pH-responsive glass electrode of composition having about 25 mol per cent Li_2O, about 2 mol per cent Cs_2O, about 2 mol per cent CaO, about 5 mol per cent BaO, about 63 mol per cent SiO_2, and about 3 mol per cent La_2O_3.

4. A pH-responsive glass electrode of composition having from about 20 to about 30 mol per cent Li_2O, 0 to about 3 mol percent Cs_2O, about 59 to about 66 mol per cent SiO_2, about 6 to about 0.5 mol per cent La_2O_3, and the remainder consisting of the oxide SrO.

5. A glass electrode having a sodium error not exceeding 1 pH at 2N sodium at 12.6 pH at temperature 25° C. to 35° C. whose voltage/pH characteristic is reproducible throughout the range 0 pH to 14 pH, and whose glass network structure is represented by the prefusion mixture consisting of silica with Li_2O and at least one of the oxides of the group consisting of CsO, Rb_2O, Na_2O, K_2O, and with at least one of the oxides of the group consisting of CaO, BaO, SrO, and high ratio of oxygen to silicon in said structure provided by inclusion in aforesaid mixture of at least one of the oxides of the group consisting of TeO_3, P_2O_5, TiO_2, ZrO_2, As_2O_5, Cb_2O_5, Ta_2O_5, ThO_2, B_2O_3 and the rare earth metal oxides.

6. A glass electrode having a sodium error not exceeding 1 pH at 2N sodium at 12.6 pH at temperature 25° C. to 35° C., whose voltage/pH characteristics is reproducible throughout the range 0 pH to 14 pH, and of composition consisting of, in mol percentages of the entire glass composition, from about 22 to about 28 per cent Li_2O with not exceeding about 3 percent additional of at least one of the oxides of the group consisting of Na_2O, Cs_2O, Rb_2O and K_2O, at least one of the oxides of the group consisting of BaO, CaO, SrO totalling not more than from about 3 percent to about 9 percent, and silica from about 59 to about 66 percent with from about .5 percent to about 6 percent of at least one oxygen modifier of the group consisting of TeO_3, P_2O_5, TiO_2, ZrO_2, As_2O_5, Cb_2O_5, Ta_2O_5, ThO_2, B_2O_3 and the rare earth metal oxides.

7. A glass electrode having a sodium error not exceeding 1 pH at 2N sodium at 12.6 pH at temperature 25° C. to 35° C., whose voltage/pH characteristic is reproducible throughout the range of 0 pH to 14 pH, and whose composition in mol percentages consists of Li_2O aggregating with at least one of the oxides of the group consisting of Cs_2O, Rb_2O, Na_2O, K_2O from about 25 percent to about 31 percent, from about 3 percent to about 9 percent of at least one of the oxides of the group consisting of BaO, CaO, SrO, a component of not more than about 6 percent of at least one of the oxygen modifiers of the group consisting of TeO_3, P_2O_5, TiO_2, ZrO_2, As_2O_5, Cb_2O_5, Ta_2O_5, ThO_2, B_2O_3 and the rare earth metal oxides, and a component of silica not exceeding about 66 per cent.

8. A pH-responsive electrode of glass having a sodium error not exceeding 1 pH at 2N sodium at 12.6 pH at temperature 25° C. to 35° C., whose voltage/pH characteristic is reproducible throughout the range 0 pH to 14 pH, and whose composition is represented by a prefusion mixture consisting af silica, lithia, at least one alkaline earth metal oxide, and at least one of the oxygen modifiers of the group consisting of TeO_3, P_2O_5, TiO_2, ZrO_2, As_2O_5, Cb_2O_3, Ta_2O_5, ThO_2, B_2O_3 and the rare earth metal oxides.

GEORGE A. PERLEY.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,311,977	Coleman	Feb. 23, 1943

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"Journal of Biological Chemistry," volume 81 (1929), page 582; article by Mirsky et al.

Certificate of Correction

Patent No. 2,444,845. July 6, 1948.

GEORGE A. PERLEY

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Column 11, line 27, claim 5, for "CsO" read *Cs_2O*; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 16th day of November, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.