

An Alternative Electrode System for Monitoring Belousov-Zhabotinsky Chemical Oscillations

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Abstract

The capability of copper-platinum (Cu/Pt) electrode system as a Belousov-Zhabotinsky (BZ) chemical oscillation monitor was compared with that of the normally used SCE/Pt electrode system, by testing it on three BZ systems, which were obtained by varying the oscillator in the combination bromate, oscillator and malonic acid. The oscillators, used separately, were cerium(IV), manganese(II) and ferroin [iron (II)-1,10-phenanthroline complex].

Cu/Pt electrode gave essentially identical values of oscillation characteristics (oscillation period, peak potential, induction period, peak width) except peak potentials. This indicated that the Cu/Pt electrode system would be more useful than the SCE/Pt electrode system (which had chloride leakage problem), in electrical applications of chemical oscillations, such as electrical switches, which would depend only on the on/off frequency.

Keywords: *Chemical oscillation, Belousov-Zhabotinsky systems, alternative electrode system, cerium (IV), ferroin, manganese(II), oscillation characteristics, oscillation monitor, SCE/Pt electrode system, Cu/Pt electrode system, electrical switches.*

Introduction

Potential oscillations accompany chemical oscillations, thus potentiometric monitoring was suitable (Win and Win 1985). The potential oscillations were traced out as peaks on a chart recorder. The time lapse between two consecutive peaks was the oscillation period (*tos*). The potential difference between base and peak maximum was the peak potential (*pp*). The time gap measured full width at half maximum, FWHM was the peak width (*pw*). The time taken for onset of oscillations after addition of the last reactant was the induction period (*tin*).

The above were collectively termed oscillation characteristics. The peak width and the peak potential were a rough indication of the potential peak shape (Win and Win 1985).

Homogeneity of the chemical system was always achieved either by magnetic stirring or gas bubbling, in both flow systems and closed static systems. Gas bubbling is preferable, as magnetic stirring tends to interfere with the relatively small potential oscillations that accompany chemical oscillations.

SCE/Pt electrode system was normally used to follow the potential variations that accompany chemical oscillations. Others, such as Polarographic and spectrometric monitors had also been used in a limited number of studies. These were presumably done because the instruments were available at hand and not intended as a study to evaluate the electrode systems.

Current interest in the Belousov-Zhabotinsky chemical oscillations was apparent in the varied publications on different aspects

of the topic, such as interest in the phenomena (Hudson and Mankin 1981); interest in three dimensional models (Field and Gyoergi 1991, 1992); publication of books (Epstein and Pojman 2000); theoretical calculations (Martin, 2001), and practical observations (Olexova *et al.* 1996) and two previous papers by the same authors (Than *et al.* 2001a,b).

In future, chemical oscillations could be developed as electro-chemical switches, which switches electric current flow on and off periodically at a fixed frequency. The normally used SCE/Pt electrode system tends to leak out chloride anions. This would interfere with the bromate functions in chemical oscillations and affect the switching frequency. Thus search for electrode systems for use as monitors in these switches was considered. It was decided to test the Cu/Pt system, which if effective would be free from leakage problem and would be much cheaper (Win and Win 1985).

Experimental

Potassium bromate, malonic acid, manganese (II) sulfate (VI), iron (II) sulfate (VI), ammonium cerium (IV) sulfate, 1.5 M sulfuric (VI) acid and 1,10-phenanthroline were of reagent grade (BDH) and used without further purification.

Standard solutions of various reagents were prepared by dissolving accurately weighed amounts of the above chemicals in exactly measured volumes of 1.5 M sulfuric (VI) acid, except for ferroin solutions which were prepared with deionized water.

A Corning pH meter was used in conjunction with platinum Pt, copper Cu and standard calomel SCE electrodes. A water-jacketed glass reactor cell was placed in a temperature-controlled thermostated water bath. The reactants were placed in separate glass vessels and placed in the above water bath to obtain the equilibrium temperature. 20.00 mL potassium bromate solution was introduced into the reactor cell and SCE/Cu or SCE/Pt electrode pair was used. Nitrogen gas was bubbled through

at a fixed rate of 25 mL per minute. This was followed by introduction of 20.00 mL malonic acid solution and 10.00 mL of oscillator solution. The stop-clock was started simultaneously. The potential out-put variations were recorded on a UV 365 chart recorder.

Three oscillators, cerium (IV), manganese (II) and ferroin [iron (II) - 1, 10-phenanthroline complex] were used separately in three different Belousov - Zhabotinsky chemical oscillation systems.

Two electrode configurations were used. The first termed "separate configuration" had Cu or SCE dipped in potassium nitrate KNO_3 solution and Pt dipped in the test solution, where chemical oscillations take place. These two solutions were electrically connected via a salt bridge. The second termed "combined configuration" had Cu or SCE and Pt, both immersed in the test solution.

The Pt electrode was connected to the "indicator" terminal and Cu or SCE was connected to the "reference" terminal of the Corning pH meter.

Results and Discussion

Tables 1, 2 and 3 show the results of monitoring the chemical oscillations produced at varying bromate levels, in the three chemical oscillation systems, using SCE / Pt and Cu / Pt electrode systems.

The results obtained by using SCE/Pt, Cu/Pt were essentially identical for oscillation period and peak shape; but the Cu/Pt peak potentials were slightly lower.

The lower peak potentials given by Cu/Pt mean that the electrode was not giving the correct potential readout. However it must be pointed out that it was not the peak potential that was of interest but the oscillation period that was of primary interest if application as electrical switches was intended. Hence these initial experiments indicated that Cu/Pt might be used in place of SCE/Pt.

Additional experiments were done. Tables 4, 5 and 6 showed the results of monitoring the chemical oscillations produced at varying malonic acid levels, in the three chemical oscillation systems, using SCE / Pt and Cu / Pt electrode systems.

These results had the same trend as the previous results mentioned above. However, it was observed that oscillations were stopped at high bromate ion concentration when using Cu / Pt in the combined configuration. Bromine gas evolution was seen. This indicated copper interference of bromate functions. This would therefore set the bromate limit for Cu/Pt.

Conclusion

The Cu/Pt electrode system could be safely used in place of the more costly SCE/Pt electrode provided the bromate level was not too high. Hence Cu/Pt electrode with nitrogen gas bubbling would be most suitable for investigations aimed at electrical applications of chemical oscillations.

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Table 1. Oscillation Characteristics in $\text{BrO}_3^- - \text{Ce}^{4+} - \text{MA}$ system at varying $[\text{BrO}_3^-]$

[KBrO ₃]/M	SCE/Pt			Cu/Pt Sep.			Cu/Pt Comb.		
	tin/s	tos/s	pp/mV	tin/s	tos/s	pp/mV	tin/s	tos/s	pp/mV
0.002	780	286	101	664	267	109	812	280	110
0.02	540	74	77	556	68	64	508	65	65
0.06	695	46	54	743	44	45	785	47	48
0.1	883	40	46	924	40	35	969	41	33
0.14	1125	33	34	1140	34	22	na	na	na
0.18	1577	28	14	1567	29	9	na	na	na

MA = malonic acid
 Cu/Pt Sep. = Separated configuration (see text) na = data not available; bromine gas evolution (see text)
 Cu/Pt Comb. = Combined configuration (see text)

Table 2. Oscillation Characteristics in $\text{BrO}_3^- - \text{Mn}^{2+} - \text{MA}$ system at varying $[\text{BrO}_3^-]$

[KBrO ₃]/M	SCE/Pt			Cu/Pt Sep.			Cu/Pt Comb.		
	tin/s	tos/s	pp/mV	tin/s	tos/s	pp/mV	tin/s	tos/s	pp/mV
0.006	232	81	46	226	81	51	266	80	54
0.02	264	84	45	258	35	45	298	36	47
0.06	344	22	43	345	23	39	385	23	40
0.1	395	20	35	395	20	29	435	20	30
0.14	445	18	20	442	18	23	na	na	na
0.18	509	16	17	517	17	19	na	na	na
0.22	590	15	16	560	16	12	na	na	na

MA = malonic acid
 Cu/Pt Sep. = Separated configuration (see text) na = data not available; bromine gas evolution (see text)
 Cu/Pt Comb. = Combined configuration (see text)

Table 3. Oscillation Characteristics in $\text{BrO}_3^- - \text{Ferriin} - \text{MA}$ system at varying $[\text{BrO}_3^-]$

[KBrO ₃]/M	SCE/Pt			Cu/Pt Sep.			Cu/Pt Comb.		
	tin/s	tos/s	pp/mV	tin/s	tos/s	pp/mV	tin/s	tos/s	pp/mV
0.01	280	50	34	272	40	44	na	na	na
0.015	320	27	13	314	25	14	374	25	10
0.02	340	12	8	334	10	7	394	10	5
0.025	380	8	6	369	7	5	429	7	3
0.03	440	7	4	439	6	3	na	na	na

MA = malonic acid
 Cu/Pt Sep. = Separated configuration (see text) na = data not available; bromine gas evolution (see text)
 Cu/Pt Comb. = Combined configuration (see text)

Table 4. Oscillation Characteristics in BrO_3^- - Ce^{4+} - MA system at varying [MA]

[MA]/M	SCE/Pt			Cu/Pt Sep.			Cu/Pt Comb.		
	tin/s	tos/s	pp/mV	tin/s	tos/s	pp/mV	tin/s	tos/s	pp/mV
0.03	883	40	46	924	40	35	969	41	33
0.2	360	13	55	396	14	43	401	14	44
0.8	880	6	36	452	6	28	455	6	29
1.2	490	5	21	538	5	18	540	5	20
1.6	715	4	8	750	4	6	750	4	7

MA = malonic acid
 Cu/Pt Sep. = Separated configuration (see text) na = data not available; bromine gas evolution (see text)
 Cu/Pt Comb. = Combined configuration (see text)

Table 5. Oscillation Characteristics in BrO_3^- - Mn^{2+} - MA system at varying [MA]

[MA]/M	SCE/Pt			Cu/Pt Sep.			Cu/Pt Comb.		
	tin/s	tos/s	pp/mV	tin/s	tos/s	pp/mV	tin/s	tos/s	pp/mV
0.01	702	33	10	722	36	16	na	na	na
0.2	173	11	40	172	12	38	187	12	39
2	90	6	28	98	6	27	113	6	30
4	80	4	23	76	4	15	90	4	14

MA = malonic acid
 Cu/Pt Sep. = Separated configuration (see text) na = data not available; bromine gas evolution (see text)
 Cu/Pt Comb. = Combined configuration (see text)

Table 6. Oscillation Characteristics in BrO_3^- - Ferriin - MA system at varying [MA]

[MA]/M	SCE/Pt			Cu/Pt Sep.			Cu/Pt Comb.		
	tin/s	tos/s	pp/mV	tin/s	tos/s	pp/mV	tin/s	tos/s	pp/mV
0.01	260	70	18	220	89	17	552	118	25
0.05	330	34	11	305	32	10	467	30	11
0.1	445	30	8	500	30	8	662	28	9

MA = malonic acid
 Cu/Pt Sep. = Separated configuration (see text) na = data not available; bromine gas evolution (see text)
 Cu/Pt Comb. = Combined configuration (see text)