Ferricyanide-Sensing Electrodes

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The Ferricyanide-sensing electrodes were prepared with Ag_2S and $Ag_3Fe(CN)_6$ (mole ratio 3:1-7:1). The 5:1 (Ag_2S:$Ag_3Fe(CN)_6$) composition is superior to others in terms of potentiometric response, rapidity of response and reproducibility. Testing was done over the concentration range 10^{-1}M~10^{-6}M $Fe(CN)_6^{3-}$ at pH 6.8 with constant ionic strength. The concentration-potential curve was linear and coincided with the Nernstian slope (19.7mV/decade). Interfering ions were I^-, Br^-, SCN^- and $Fe(CN)_6^{4-}$ and the life time of this electrode was 3 weeks. This electrode could be used as the indicator electrode for measuring the ferricyanide and ferrocyanide.

Introduction

The ion selective electrodes,[1,2] developed for the first time by Cremer[3] in 1906, have been widely used for the determination of quantities of component in the field of pollution,[4,5] medicine,[6] biochemistry,[7] and analytical chemistry.[8] These electrodes are classified into liquid membrane electrodes,[9-10] solid membrane electrodes,[11,12] and gas sensing electrodes.[13-15]

In particular, the solid state membrane electrodes have been remarkably progressed. Recently, the solid membrane electrodes on the salts of oxygen acid, such as antimony oxide,[16] chromate[17] and sulfate[18] have been reported by many authors, but electrode on the complex ion has been rarely reported. And although a number of methods are available for the determination of ferricyanide, up to the present, there have been no reports of the methods that are used directly by the ferricyanide ion selective electrodes.

In this paper, ferricyanide sensing electrodes were prepared by mixing silver sulfide-silver ferricyanide and then tested for sensitivity, life time and interferences.

Experiments

1. Apparatus and Reagents

The ferricyanide-sensing electrodes prepared in our laboratory were used as the indicator electode, the reference was the saturated calomel electrode (porous plug type, Fisher Co.). An Orion Research Model #901 Digital microprocessor ionalyzer was used for potential measurements. The pH of the solution was measured on an Orion Research Model #611 Digital pH meter with a combined glass calomel electrode. A Carver Laboratory Press (Model C-29000-378) was used for the preparation of pellets. Silver nitrate, potassium ferricyanide and ammonium chloride were obtained from Wako Chemical Co., silver wire and silver powder were obtained from Alfa Division Ventron.

2. Preparation of electrodes

The powder of the active materials (Ag_2S and $Ag_3Fe(CN)_6$, 0.8g) and silver powder (0.4g) were pressed on the press for 10 hours, at 10 ton/cm^2. The silver wire was fixed on the silver plate of the pellet, and the pellet was attached to the top of P.V.C tube by epoxy resin such as Figure 1.

3. Analytical procedures

In order to measure the sensitivity of ferricyanide from sample solution, ferricyanide sensing electrode and reference electrode were soaked in the 30 ml sample, which was stirred at 600 rpm by magnetic bar at 25°C. The measuring system is shown in Figure 2.

Result and Discussion

1. The responses of electrodes

The measured results of various concentration of ferri-

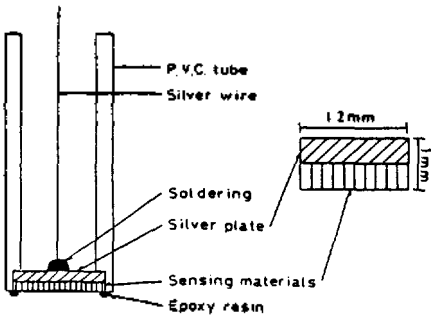

Figure 1. Designs for ferricyanide sensing electrode and pellet.

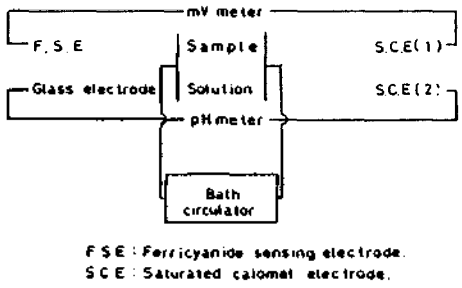

Figure 2. The measuring system.

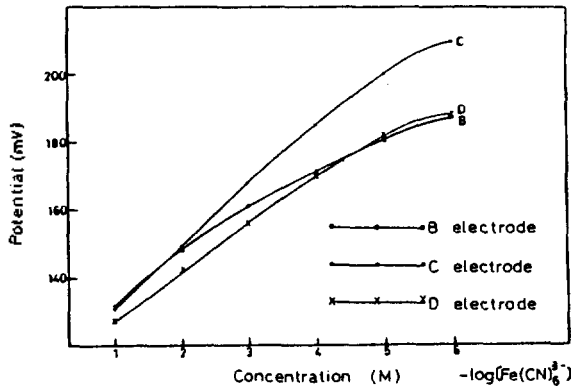

Figure 3. Response curves for ferricyanide ion.

Table 1. Responses for ferricyanide ion

Electrodes NO.	Ag_2S : $Ag_3Fe(CN)_6$ mole ratio	Pressing		$Fe(CN)_6^{3-}$ Response (mV, negative slope)	
		Pressure	Time		
A	3 : 1	10Tons	10hr	11.9-10.4	10^{-1}M-10^{-3}M
				8.8- 6.3	10^{-3}M-10^{-5}M
B	4 : 1	10Tons	10hr	16.0-13.0-10.1	10^{-1}M-10^{-4}M
				9.3- 6.9	10^{-4}M-10^{-6}M
C	5 : 1	10Tons	10hr	19.7-18.1-17.1	10^{-1}M-10^{-4}M
				15.2-10.8	10^{-4}M-10^{-6}M
D	6 : 1	10Tons	10hr	16.7-13.6-13.3	10^{-1}M-10^{-4}M
				12.1- 8.4	10^{-4}M-10^{-6}M
E	7 : 1	10Tons	10hr	12.1-10.7	10^{-1}M-10^{-3}M
				9.8- 7.2	10^{-3}M-10^{-5}M

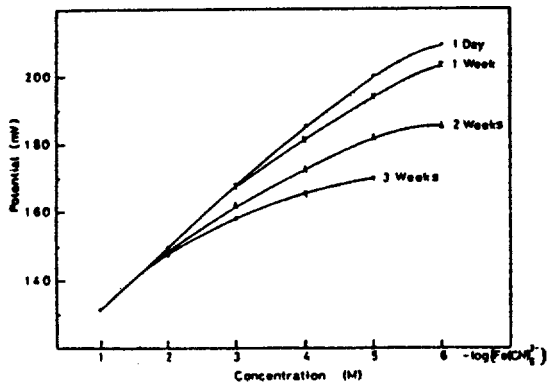

Figure 4. The life time of the electrode.

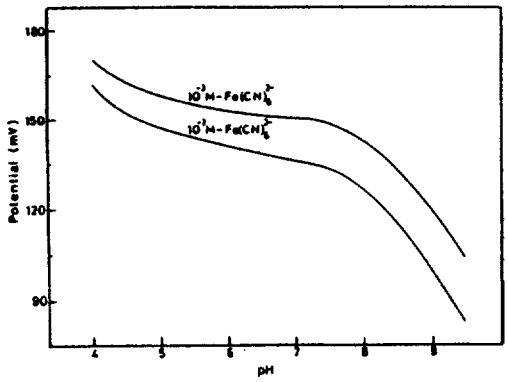

Figure 5. The effect of pH on the ferricyanide ion.

cyanide solution using the prepared ferricyanide ion selective electrodes are given in Table 1 and Figure 3.

The dependence of the electrode potential on the ferricyanide concentration was tested in potassium ferricyanide solution in the range 10^{-1}M–10^{-6}M, at pH 6.8 with constant ionic strength. As the results show, the 5:1 (mole ratio of Ag_2S and $Ag_3Fe(CN)_6$) composition is superior to others in terms of potentiometric response. Figure 3 shows that the concentration-potential curves were linear and coincided with the Nernstian slope (19.7mV/decade). And the life time of this electrode was 3 weeks, as shown in Figure 4.

2. The effect of pH

The effect of pH was observed in solution of 10^{-2}M, 10^{-3}M ferricyanide. The pH was adjusted by addition of sodium hydroxide or acetic acid. The resulting potentials were plotted against pH in Figure 5. It is noted in Figure 5 that the potential resposne of the ferricyanide is not seriously affected by pH 5.5–7.5.

Table 2. Interferences

Interferences	Concentration(M)	Response(mV)	ΔmV
F^-	1 × 10^{-2}	151.5	0
Cl^-	1 × 10^{-2}	151.5	0
I^-	1 × 10^{-2}	81.3	- 70.2
Br^-	1 × 10^{-2}	69.2	- 82.3
S^{2-}	1 × 10^{-2}	79.5	- 72.0
SCN^-	1 × 10^{-2}	90.8	- 60.7
HCO_3^-	1 × 10^{-2}	151.5	0
SO_4^{2-}	1 × 10^{-2}	151.5	0
$C_2O_4^{2-}$	1 × 10^{-2}	151.5	0
HPO_4^{2-}	1 × 10^{-2}	151.5	0
WO_4^{2-}	1 × 10^{-2}	151.5	0
CrO_4^{2-}	1 × 10^{-2}	151.5	0
$HAsO_3^{2-}$	1 × 10^{-2}	151.5	0
$Fe(CN)_6^{4-}$	1 × 10^{-2}	116.3	-35.2
None	1 × 10^{-2}	151.5	0

3. Interferences

The influence of interfernces was determined in the sample solution containing various interfering ions.

As the results, Table 2 shows that interfering ions are iodide, bromide, sulfide, thiocyanate and ferrocyanide ion, but other ions are not interfered.

4. Potentiometric titration

The electrode (#C) also has been used as an indicator electrode in the analytical titration. The titration curve of 20 ml of 10^{-2}M ferricyanide with 10^{-1}M silver nitrate standard solution is shown in Figure 6.

Similarly, the titration curve of 10^{-3}M ferricyanide with 10^{-2}M silver nitrate standard solution is shown in Figure 7. The each inflection point may be taken as the end point.

Figure 8 is the curves that are titrated 10^{-2}M ferricyanide and ferrocyanide with 10^{-1}M silver nitrate standard solution. Precipitation of silver ferricyanide occurs after silver ferrocyanide precipitates in the mixture. Therefore, the first inflection point is the equivalent point of ferrocyanide, the second is that of ferricyanide.

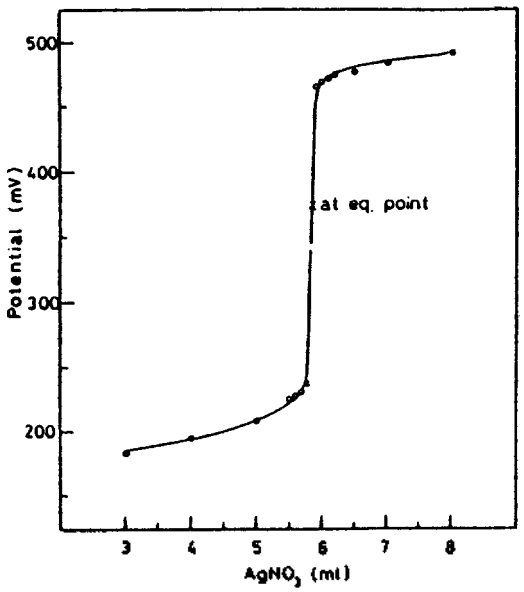

Figure 6. The potentiometric titration curve of 10^{-2}M-$Fe(CN)_6^{4-}$ 20 m*l* with 10^{-1}M-$AgNO_3$.

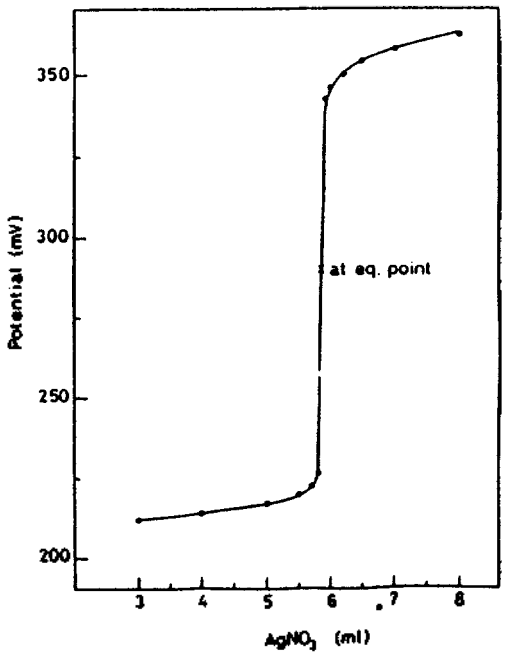

Figure 7. The potentiomtric titration curve of 10^{-2}M-$Fe(CN)_6^{4-}$ 20 m*l* with 10^{-2}M-$AgNO_3$.

Conclusions

1. The ferricyanide sensing electrodes have been prepared with Ag_2S and $Ag_3Fe(CN)_6$ (mole ratio 3:1-7:1).
2. The 5:1 composition is superior to others in terms of response. Testing was done over the concentration range 10^{-1}M-10^{-6}M ferricyanide.
3. The best stable pH range was pH 5.5-7.5.
4. Interfering ions were I^-, Br^-, S^{2-}, SCN^- and $Fe(CN)_6^{4-}$.
5. The life time of the electrode was 3 weeks.
6. This electrode was used as the indicator electrode in potentiometric titration of ferricyanide and ferrocyanide.

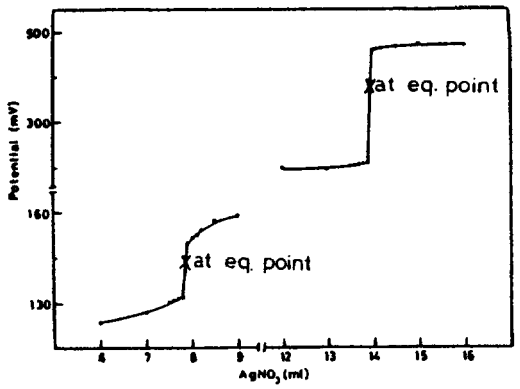

Figure 8. The potentiometric titration curve of 10^{-2}M-$Fe(CN)_6^{4-}$ 20 m*l* and 10^{-2}M-$Fe(CN)_6^{4-}$ 20 m*l* with 10^{-1}M-$AgNO_3$.

References

1. R.B. Fischer, *Chem. Edu.*, **51** (6), 387 (1974).
2. J.P. Sapis and R.D. Braun, *Chemistry*, **46** (6),14 (1973).
3. Cremer; *Z., Boil.*, **47**, 562 (1906).
4. P.J. Cusbert, *Anal. Chim. Acta*, **87**, 429 (1976).
5. E.W. Bauman, *Anal. Chem.*, **46**, 1345 (1974).
6. P.W. Alexander and G.A. Rechnitz, *Anal. Chem.*, **46**, 250 (1974).
7. A.H. Truesdell and A.M. Pommer, *Science*, **142**, 1292 (1963).
8. Daniel Jangner and J.P. Ostergaard Jensen, *Anal. Chim. Acta*, **80**, 9 (1975).
9. R.W. Cattrall and D.M. Drew and J.C. Hamilton, *ibid.*, **76**, 269 (1975).
10. R.W. Cattrall and D.M. Drew, *ibid.*, **77**, 9 (1975).
11. D.J. Crombie, G.J. Moody, *ibid.*, **80**, 1 (1975).
12. J.W. Ross and M.S. Frant, *Anal. Chem.*, **41** (7), 967 (1969).
13. L.R. Mckenzie and P.N.W. Young, *Analyst*, **100** (9), 620 (1975).
14. M. Meyerhoff and G.A. Rechnitz, *Anal. Chim. Acta*, **85**, 277 (1976).
15. P.K. Kobos and G.A. Rechnitz, *Anal. Lett.*, **10** (50), 751 (1977).
16. E. Edwall, *Med. biol. Eng. Comp.*, **16** (6), 661 (1978).
17. E.J. Hakoila, U.O. Lukkari, H.K. Lukkari, and A. Takala, *Acta Chem. Fenn.*, **46** (11-12), 1973.
18. J.O. Jasinki, and I. Trachtenberg, *Anal. Chem.*, **44**, 2373 (1972).