

DEVELOPMENT OF AN AMPEROMETRIC SENSOR FOR POTASSIUM IONS

Marcos F. S. Teixeira, Alex S. Lima, Patricia Monteiro Seraphim

*Dep. of Physical, Chemistry and Biology, Faculty of Science and Technology, University of State of Sao Paulo (UNESP)
Rua Roberto Simonsen, 305 - Presidente Prudente – SP - Brazil*

Nerilso Bocchi

*Department of Chemistry, Federal University of São Carlos
Via Washington Luiz, Km 235 - São Carlos – SP - Brazil*

Keywords: Sensor for potassium ions, hollandite, voltammetry.

Abstract: Hollandite-type manganese oxides are nanofibrous crystals with sub-nanometer open tunnels that provide a unique property for sensing applications. Sensor based on hollandite-type manganese oxide was investigated for amperometric detection of potassium. With an operating potential of +0.63 V *versus* SCE, potassium ions produce oxidation currents at the sensor, which can be exploited for quantitative determinations. The amperometric signals are linearly proportional to potassium ions concentration in the range 2.7×10^{-4} to 9.1×10^{-4} mol L^{-1} with a correlation coefficient of 0.9990. The construction and renewal are simple and inexpensive.

1 INTRODUCTION

Determination of potassium contents of serum, urine, and foods is very important in clinical and medical fields, since the potassium contents are related to renal diseases. These diseases restrict patients to a diet containing a large amount of potassium. From the potassium determination, medical information concerning physical conditions of the patient can be obtained. In the case of hypopotassemia, alkalosis, cirrhosis of liver, diuretic drugs, etc. are suspected. On the other hand, when potassium concentration in human serum becomes higher than 9 mmol L^{-1} , heart often stops (Harrison *et al.*, 1966). Hence, accurate, easy and rapid sensing of potassium ions is very important.

The development of chemical sensors for non-electroactive ions based with modified electrodes has been based in the participation of non-electroactive cations in redox reactions of metal hexacyanoferrates (Karyakin, 2001). Other compound with ability of accommodate non-electroactive cations and promote the electroactivity in function of the insertion cation is the manganese oxide. Manganese oxides represent a large class of materials that have layered and tunneled structures

consisting of edge-shared MnO_6 octahedral units. They have attracted considerable interest due to broad potential applications in heterogeneous catalysis, chemical sensing, toxic wastewater treatment, and rechargeable battery technology. In our laboratories, we are also interested in developing highly sensitive and selective methods for the determination of non-electroactive using electrodes modified with different allotropic forms of manganese oxide (Teixeira *et al.*, 2004 and Teixeira *et al.*, 2004).

In this paper, we propose a new sensor to determine potassium ions.

2 EXPERIMENTAL

2.1 Apparatus

All voltammetric measurements were carried out in a 30ml thermostated glass cell at 25°C , containing three electrodes: carbon-paste electrode as a working electrode, saturated calomel as reference electrode (SCE), and platinum wire as an auxiliary electrode. During the measurements, the aqueous solution (TRIS buffer solutions) in the cell was not stirred

and deaerated. Voltammetric measurements were performed with a micro-Autolab Type III controlled by an appropriated software.

2.2 Reagents and Solutions

All solutions were prepared using a Millipore Milli-Q water. All chemicals were analytical reagent grade and were used without further purification. The supporting electrolyte used for most of the experiments was a 0.1 mol l⁻¹ Tris buffer solution (pH = 8.30). A 0.01 mol l⁻¹ potassium ions solution was prepared daily by dissolving potassium chloride (Merck) in 100 ml of such Tris buffer solution. Graphite powder (1–2 μm particle size from Aldrich) and mineral oil (Aldrich) of high purity were used for the preparation of the sensor.

2.3 Preparation of Hollandite-Type MnO₂

Hollandite-type manganese(IV) oxide was prepared using a reflux method according to literature (Ching *et al.* 1997). For conversion to hollandite-type manganese oxide, a KMn₂O₄ sample was treated in an aqueous diluted sulfuric acid solution kept under constant stirring during 120 min. When the pH of this mixture was stabilized at a particular value, the solution was decanted and the remaining solid material washed by decantation with deionized water, filtered and dried in air at 90°C.

2.4 Sensor Construction

Sensors with hollandite-type MnO₂ were prepared by carefully mixing the dispersed graphite powder with manganese oxide at varying ratio. Exactly 1 g of this mixture was subsequently added to 0.200 g of mineral oil (20% m/m) and mixed in a 50 ml beaker containing 20 ml of hexane. The final paste was obtained with the solvent evaporation. The carbon-paste electrode was finally obtained packing the paste into a plastic tube (1 ml insulin plastic syringe) and arranged with a copper wire serving as an external electric contact.

3 RESULTS AND DISCUSSION

3.1 Electrochemical Behavior

First, the voltammetric behavior of the CPEM with hollandite-type manganese oxide in Tris buffer

solution (pH 8.3) containing 5.0 × 10⁻⁴ mol L⁻¹ potassium ions was investigated. The cyclic voltammograms obtained with the sensor (see Fig. 1) presented one anodic peak (peak I = 0.63 V vs. SCE) and another cathodic peak (peak II = 0.08 vs. SCE). This electrochemical activity is due to the extraction topotactic process of the potassium ions from the hollandite structure, which occurs in two steps to the electrochemical insertion/extraction processes of the potassium ions (Feng *et al.*, 1995):

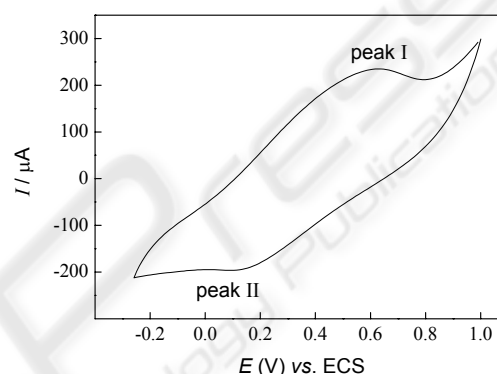
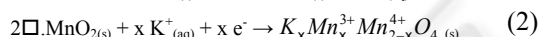
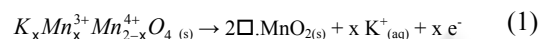
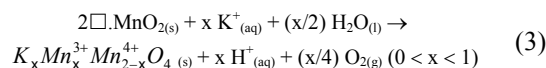


Figure 1: Cyclic voltammogram of the sensor in 5.0 × 10⁻⁴ mol L⁻¹ of potassium ions, at a scan rate of 50 mV s⁻¹ between - 0.15 and 1.00 V versus SCE.

The enhanced response to potassium ions occurs because the cathodic polarization of the sensor with hollandite-type manganese oxide is quite enough to reduce the manganese in the solid. Consequently, the potassium ions from the adjacent solution are able to diffuse through the hollandite structure to maintain the electroneutrality principle.

In the absence of potassium ions, no voltammetric response was observed for the sensor, confirming that the response of the sensor is a function of the insertion reaction of potassium ions in the hollandite structure as mentioned previously (see Eq. 3):



where \Box is vacant site (tunnel) of the manganese oxide.

The apparent electrochemical rate constant k_e and the electron-transfer coefficient α_{anodic} were calculated for the sensor according to the method described by Larivon (Larivon, 1979). It has been shown by Larivon that for a surface redox couple, α_{anodic} and k_e can be determined from the variation of E_{pa} with scan rate. Figure 2 presents the plot of E_{pa} (V)

versus $\log v$ ($V s^{-1}$) of the sensor in Tris buffer solution (pH 8.3) containing $5.0 \times 10^{-4} \text{ mol L}^{-1}$ potassium ions. For large enough values of scan rate the $E_p - \log v$ plots gave one straight line with slopes of $2.303RT/(1 - \alpha_{\text{anodic}})nF$ for the anodic branch, where R is the gas constant, T the absolute temperature, F the Faraday constant and n number of electrons involved in the redox couple. Considering that the number of electrons involved in the redox process is 1, the calculated value for the coefficient α_{anodic} was 0.83. These results suggest the redox process tends towards an irreversible system. The apparent electrochemical rate constant can then be determined applying the equation $k_e = 2.303\alpha_{\text{anodic}}nFv_0/RT$, in which the value of scan rate (v_0) is determined by extrapolation of the linear branch at higher scan rates and its intersection with the constant peak potential, represented by the peak of the voltammogram at the lower scan rate. The observed value was $k_e = 32.2 \text{ s}^{-1}$.

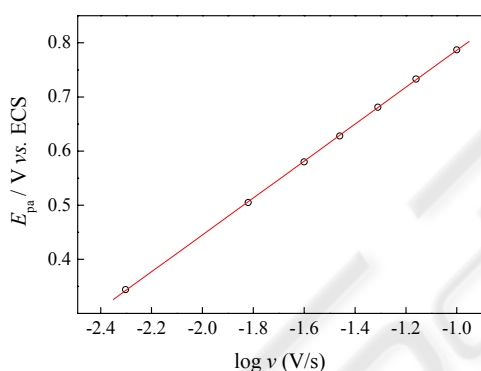


Figure 2: Dependence of E_{pa} with $\log(v)$ for the sensor in Tris buffer solution (pH 8.3) containing $5.0 \times 10^{-4} \text{ mol L}^{-1}$ potassium ions.

The effect of the carbon paste composition in the amperometric response of the sensor was evaluated in Tris buffer solution (pH 8.3) containing $5.0 \times 10^{-4} \text{ mol L}^{-1}$ potassium ions. The anodic peak current increased with the amount of manganese oxide in the paste up to 25% (m/m). The anodic peak current decreased significantly when more than 25% is used in the electrode preparation. This probably occurs due to a decrease in the conductive area at the sensor surface. According to these results a sensor composition of 25% (m/m) modified hollandite-type manganese oxide, 55% (m/m) graphite and 20% (m/m) mineral oil was used in further studies.

3.2 Analytical Curve and Repeatability

After optimizing the best operating conditions for the sensor (scan rate of 20 mV s^{-1}), cyclic voltammeteries were carried out in Tris buffer solution containing different potassium ion concentrations in order to obtain the analytical curve for such electrode. This curve, illustrated in the Figure 3, was constructed using the anodic peak currents resulting a linear relationship with the potassium ion concentrations from 2.7×10^{-4} to $9.1 \times 10^{-4} \text{ mol L}^{-1}$ ($I_{pa} (\mu A) = 2.07 + 200.8 [K^+] (\text{mol L}^{-1})$; $r = 0.9990$) with a detection limit of $1.5 \times 10^{-4} \text{ mol L}^{-1}$ potassium ions. The precision of the method was also tested by analyzing five replicates containing $5.0 \times 10^{-4} \text{ mol L}^{-1}$ potassium ions. For each voltammogram, the surface of the sensor was renewed. The variation coefficient was 2.0 %.

4 CONCLUSIONS

As shown above, a sensor based on the hollandite-type manganese oxide exhibits an obvious response to potassium ions. It is necessary to investigate the interaction mechanism between potassium ion and the hollandite-type manganese oxide. The presence of Mn^{3+} in hollandite may increase its activity for the reaction. During the amperometric detection, potassium ions diffuse through the hollandite structure to produce Mn^{3+} , which can be electrochemically reoxidized to Mn^{4+} . The oxidative current is directly related to the concentration of potassium ions. In view of its sensitivity, stability, low working potential and simplicity and low cost of construction, the sensor based on the hollandite-type manganese oxides exhibits prospects for future biosensor work.

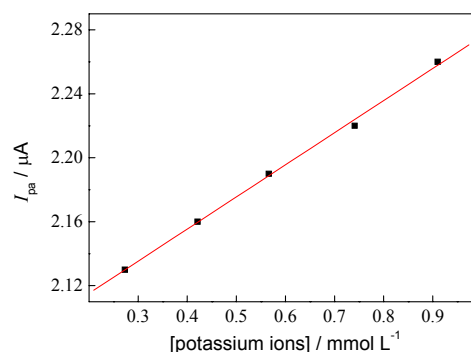


Figure 3: The curve analytical obtained from the anodic currents using sensor based hollandite-type manganese oxide.

ACKNOWLEDGEMENTS

The research support from FAPESP under contract no. 05/01296-4 and also grant by CNPq (no. 372010/2006-7) to A.S.L. are gratefully acknowledged (SJT).

REFERENCES

- Ching, S., Roark, J.L., Duan, N., Suib, S.L., 1997. *Chem. Mater.* 9, 750.
- Feng, Q., Kanoh, H., Miyai, Y., Ooi, K., 1995. *Chem. Mater.* 7, 148.
- Harrison, T.R., Adams, R.D., Bennett, I.L., Resnik, W.H., Thorn, G.W., Wintrobe M.M., (Eds.), 1966. *Principles of Internal Medicine*, 5th edn., McGraw-Hill, New York.
- Larivon, E., 1979. *J. Electroanal. Chem.* 101, 19.
- Karyakin, A.A., 2001. *Electroanalysis* 13, 813.
- Teixeira, M.F.S., Cavalheiro, E.T.G., Bergamini, M.F., Moraes, F.C., Bocchi, N., 2004. *Electroanalysis* 16, 633.
- Teixeira, M.F.S., Bergamini, M.F., Bocchi, N., 2004. *Talanta* 62, 603.

