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A SECONDARY CELL BASED ON THIN LAYERS OF ZEOLITE-LIKE NICKEL HEXACYANOMETALLATES

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Abstract—Thin layers on Ni of nickel hexacyanoferrate (NiHCFe) and on Pt of nickel hexacyanoruthenate (NiHCRu) are prepared by electrochemical deposition and studied with respect to their charge storage characteristics. Cyclic voltammetry shows highly reversible behaviour, except for NiHCRu at potentials larger than *ca* 1.0 V *vs sce* where parasitic oxidation processes occur. Cycling of single electrodes as well as of a cell with NiHCFe as anode and NiHCRu as cathode exhibits a current efficiency of nearly 100% and a decrease of charge capacity with increasing cycle number. The latter fact is traced back to the layers being not completely insoluble in the electrolyte, to structural changes during cycling, and to the parasitic processes occurring at NiHCRu. Possibilities for improvement of the electrodes, particularly concerning stability and enlargement of the charge capacity of the cell, are discussed.

INTRODUCTION

It is a well known fact that intercalation compounds represent highly reversible electroactive materials[1]. Thus the zeolite-like and insoluble hexacyanometallates such as Prussian blue, which upon reduction reversibly insert cations[2], should exhibit charge storage characteristics. Until now, however, the main interest of reports on hexacyanometallate-modified electrodes was directed to electrochromic[4–7], electrocatylytic[8–10], and ion-selective[11, 12] behaviour. A secondary cell with Prussian blue layers on porous graphite was described for the first time by Neff[13]. In this system, however, the electrodes suffered from low mechanical stability leading to rapid decrease of charge capacity. In another approach[14] thin layers on platinum of iron hexacyanoferrate (FeHCFe) and of copper hexacyanoferrate (CuHCFe) were used as anodes and cathodes, respectively, in a secondary cell. Although the films were stable enabling more than 1000 cycles without decrease of current efficiency, the charge capacity was small and the base metal used expensive. Thus films of nickel hexacyanoferrate (NiHCFe) and of nickel hexacyanoruthenate (NiHCRu) on nickel electrodes were studied. The intention was that, once these films give stable and reversibly operating electrodes, an enlargement of cell capacity by using stacks of metal-deposited polymer foils might readily be possible.

A secondary cell with NiHCFe as anode and NiHCRu as cathode can be schematically represented by the reaction:

$$Na_2NiFe^{II}(CN)_6 + NaNiRu^{III}(CN)_6 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} NaNiFe^{III}(CN)_6 + Na_2NiRu^{II}(CN)_6. \qquad (1)$$

Besides the redox reaction in the electrodes, the only process that occurs during cycling is the movement of Na^+ ions from one electrode to the other *via* the electrolyte. The theoretical capacity of such a cell amounts to 78 mAh cm^{-3}. With a thermodynamic cell voltage of 0.5 V, this gives an energy density of 39 mWh cm^{-3} which is twice that of a redox battery such as 1 M Ti^{3+}/Fe^{2+}[15].

EXPERIMENTAL

Disks of Ni and Pt sealed into glass tubes and polished by using 1 μm diamond spray served as electrodes. For measurements with single electrodes conventional three-electrode cells were taken. For measurements on a secondary cell, the four-electrode arrangement shown in Fig. 1 with two working electrodes, counter electrode (Pt wire), and reference electrode was used. Thus it was possible to take voltammograms at distinct time intervals during charge-discharge cycling without the need of changing the cell. A saturated calomel electrode (*sce*) served as reference electrode.

A potentiostat/galvanostat (Jaissle model 2002) combined with a computer-controlled voltage generator (Jaissle DAC 12 B, Siemens PC 100) was used for film preparation and voltammetric measurements. Charge-discharge curves were taken by using a galvanostat (Amel model 545), and the charge was measured by means of an integrator (Tacussel model IG 6 N).

All Chemicals (Alfa, Fluka) were of p.a. or purissimum quality and used as obtained. Solutions were prepared with double distilled water and deaerated by nitrogen bubbling.

The preparation of NiHCFe films on Ni was conducted by potentiostatic oxidation at 1.1 V *vs sce* in an aqueous solution of 5×10^{-3} M $K_3Fe(CN)_6$ and 0.1 M $NaClO_4$. NiHCRu films on Pt were prepared by cathodic deposition of Ni from a Watts bath (0.84 M $NiSO_4 \cdot 6H_2O$, 0.25 M $NiCl_2 \cdot 6\,H_2O$, 0.61 M H_3BO_3, pH 3.5–4.2) and subsequent potentiostatic oxidation at 1.25 V *vs sce* in an aqueous solution of 5×10^{-3} M $K_4Ru(CN)_6$ and 0.1 M $NaClO_4$.

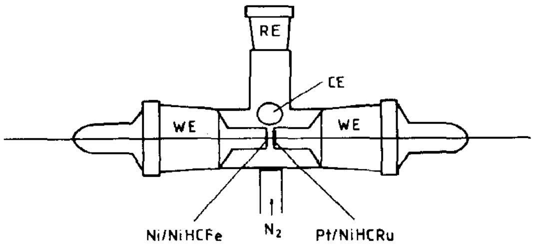


Fig. 1. Four-electrode arrangement for taking voltammograms in the same cell as that used for two-electrode cycling experiments. WE: working electrodes (Ni/NiHCFe and Pt/NiHCRu, respectively); CE: counter electrode (Pt); RE: reference electrode (*sce*).

The NiHCRu films obtained were relatively thin (0.1 mC cm^{-2}) since a large portion of the oxidation current was consumed by the oxidation of $Ru(CN)_6^{4-}$ to $Ru(CN)_6^{3-}$. Therefore the NiHCRu electrodes were cycled repeatedly over the redox wave in 0.1 M $NaClO_4$ solution containing 10^{-4} M $K_4Ru(CN)_6$. This procedure was called "forming" and led to an enlargement of the films' charge capacity by more than 100%. The NiHCFe films were "formed", too, but the forming resulted in a stabilization of the film only and not in an increase of the charge capacity.

All experiments were performed at room temperature.

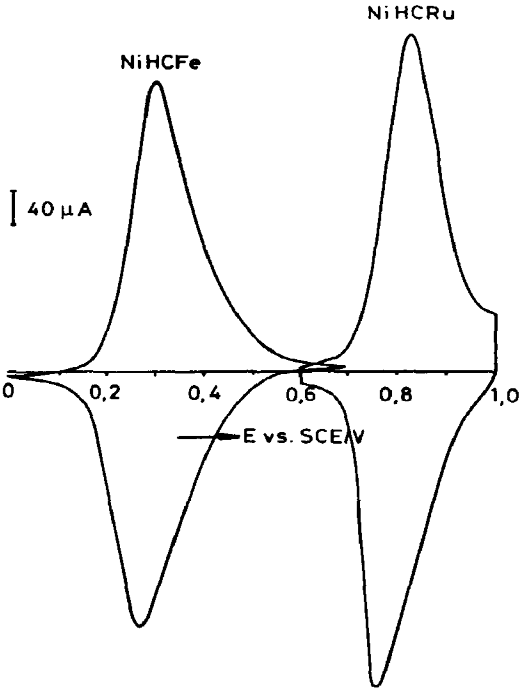


Fig. 2. Cyclic voltammograms of thin layers of NiHCFe and NiHCRu. Electrolyte: 0.1 M $NaClO_4$; voltage scan: 50 mV s^{-1}; coating: 2.1 mC cm^{-2} (NiHCFe), 0.8 mC cm^{-2} (NiHCRu); area: 0.5 cm^2.

RESULTS AND DISCUSSION

Voltammetry

Typical cyclic voltammograms of films of NiHCFe (left curve) and of NiHCRu (right curve) are shown in Fig. 2. The voltammograms were taken separately and combined in Fig. 2 for comparison. Starting at a potential of about 0.7 V *vs sce*, where NiHCFe is in its oxidized state, a potential scan in the negative direction converts the layer to the reduced state:

$$NaNiFe^{III}(CN)_6 + Na^+ + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Na_2NiFe^{II}(CN)_6. \quad (2)$$

Similarly the NiHCRu layer is oxidized upon scanning the potential from 0.6 to 1.0 V *vs sce*:

$$Na_2NiRu^{II}(CN)_6 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} NaNiRu^{III}(CN)_6 + Na^+ + e^-. \quad (3)$$

According to Equations (2) and (3), charging of NiHCFe is associated with uptake of Na^+ from the electrolyte whereas charging of NiHCRu is associated with release of Na^+; the reverse processes occur upon discharging.

The symmetry of the voltammograms with respect to the potential axis and to the peak current reflects the highly reversible character of the redox reactions and of the associated insertion process. The peak potential for NiHCFe is at 0.3 V *vs sce* and for NiHCRu at 0.8 V *vs sce*. The difference of the peak potentials (about 0.5 V) corresponds to the thermodynamic cell voltage of a cell with NiHCFe as anode and NiHCRu as cathode. The maximum cell voltage at full charge is 1 V.

Integration of the cyclic voltammograms gives the charge capacity of the layer. The ratio of the cathodic to the anodic charge is 1 for NiHCFe. For NiHCRu this ratio depends on the scan rate, becoming smaller with decreasing scan rate. This means that, at low scan rates, the amount of charge consumed during the oxidation and charging of the NiHCRu film is larger than the amount of charge consumed during the back reduction and discharging. We explain this effect by the fact that at potentials positive of the peak potential some parasitic oxidation processes occurs at the NiHCRu film as revealed by the cyclic voltammogram (Fig. 2, right curve): the current does not drop to zero at positive potentials (1.0 V *vs sce*) as would be expected from theory[16]. At low scan rates these parasitic and irreversible processes such as the oxidation of the solvent water and/or of the Ni substrate would be more pronounced than at higher scan rates.

It is supposed that also the forming process (see Experimental) is associated with this irreversible oxidation of the Ni substrate: Ni^{2+} ions diffuse through the film, react with $Ru(CN)_6^{4-}$ at the surface, and thus cause the growing of the film and the increase of charge capacity.

Charging and discharging

Figure 3 shows charge-discharge curves obtained from potential-limited cycling of single NiHCFe and NiHCRu electrodes (potential limits: 0.7–0 V *vs sce* for NiHCFe and 0.6–1.0 V *vs sce* for NiHCRu).

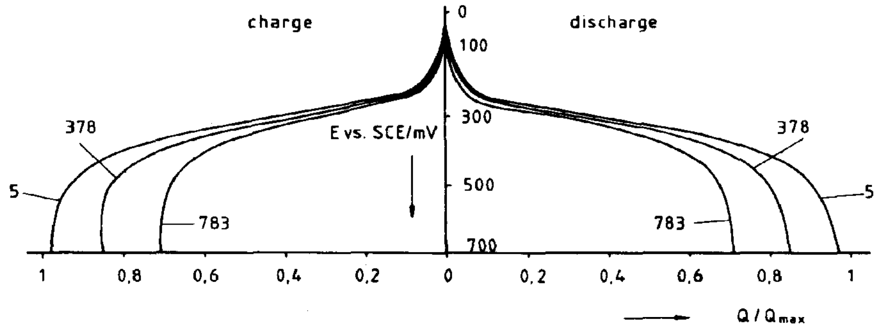
The current efficiency, defined as the ratio of the time of discharging to the time of charging at constant current, is 1 for both electrodes at all cycles. However, the exploitation of charge, which is measured by the quantity Q/Q_{max} (Q: actual charge consumed upon charging or discharging, Q_{max}: maximum available charge as obtained from a cyclic voltammogram prior to cycling), decreases with increasing cycle number. This is depicted more clearly in Fig. 4 where results for Ni/NiHCFe and Pt/NiHCRu electrodes are compared with results for NiHCFe and NiHCRu layers deposited on metallized (Ni, Pt) polycarbonate foils. After 500 cycles the charge capacity of the "compact" electrodes decays to 89% (Pt/NiHCRu) and 84% (Ni/NiHCFe), whereas that of the foils electrodes decays to 75% (Pt/NiHCRu) and 73% (Ni/NiHCFe).

The charge–discharge characteristics of a complete cell Ni/NiHCFe/0.1 M $NaClO_4$/NiHCRu/Pt are presented in Fig. 5. Although the current efficiency amounts to about 100% at all cycles, the charge capacity decreases by nearly 40% in the course of 86 cycles between 0.25 and 0.9 V.

The striking fact revealed by Figs 3–5 is the decrease of charge capacity of the hexacyanometallate electrodes upon cycling. We believe that three reasons may be responsible for this detrimental property. First, we must consider the films to be not totally insoluble. Rather during cycling a substantial amount of the films can dissolve in the electrolyte thus diminishing the charge capacity of the electrodes.

Secondly, there may be structural changes of the films during cycling. We observed an decrease of the symmetry of the voltammograms simply upon standing of the films in contact with the aqueous electrolyte. Since drying of the films restores the original voltammograms obtained prior to prolonged standing in the electrolyte, we attribute the change of symmetry of the voltammograms to reversible structural changes occuring upon prolonged contact of the films with the aqueous electrolyte. These structural changes appar-

(a) Ni/NiHCFe



(b) Pt/NiHCRu

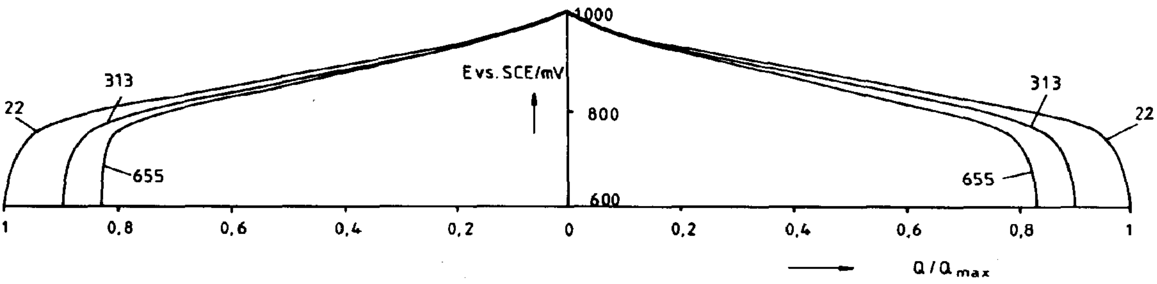


Fig. 3. Charge–discharge characteristics of a Ni/NiHCFe (a) and a Pt/NiHCRu (b) electrode. Numbers indicate cycles. Electrolyte: 0.1 M $NaClO_4$; current density: 0.1 mA cm^{-2}; potential limits: 0.7–0.0 V *vs sce* (NiHCFe) and 0.6–1.0 V *vs sce* (NiHCRu); Q_{max}: 0.9 mC cm^{-2} (NiHCFe) and 2.1 mC cm^{-2} (NiHCRu).

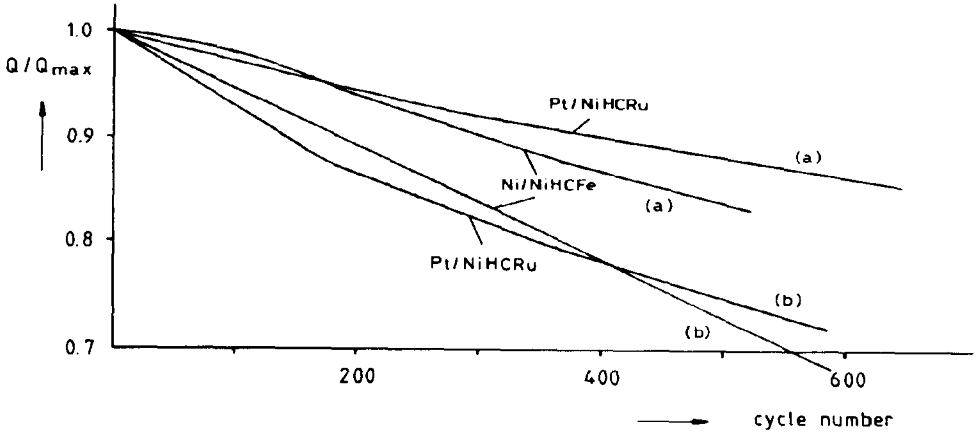


Fig. 4. Normalized charge capacity Q/Q_{max} as a function of the cycle number for NiHCFe and NiHCRu films deposited on compact metals (a) and on metallized foils (b). Metal was Ni for NiHCFe and Pt for NiHCRu, respectively. Electrolyte: 0.1 M $NaClO_4$; current density: 0.1 mA cm^{-2}; potential limits: 0.7–0.0 V (NiHCFe) and 0.6–1.0 V (NiHCRu); Q_{max}: NiHCFe: 0.9 mC cm^{-2} (compact) and 0.7 mC cm^{-2} (foil), NiHCRu: 2.1 mC cm^{-2} (compact) and 0.3 mC cm^{-2} (foil).

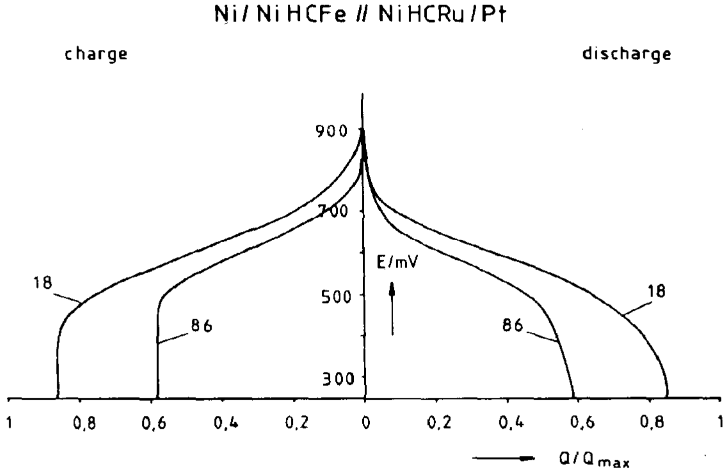


Fig. 5. Charge–discharge characteristics of the cell Ni/NiHCFe/0.1 M $NaClO_4$/NiHCRu/Pt. Numbers indicate cycles. Electrolyte: 0.1 M $NaClO_4$; current density: 0.1 mA cm^{-2}; Q_{max}: 2 mC cm^{-2} (NiHCFe), 1.3 mC cm^{-2} (NiHCRu).

ently also happen during cycling and thus contribute to the decrease of charge capacity.

Thirdly, in the case of NiHCRu, the parasitic side reactions at positive potentials mentioned above (see Fig. 2, right curve) may decrease the charge capacity in this system. We suppose that oxidation of the Ni substrate metal involving incorporation of Ni^{2+} in the film leads to a decrease of the number of sites in the film which must be available for the insertion of Na^+ ions upon reduction. Thus an additional reduction of charge capacity of NiHCRu films is caused.

Finally, it should be mentioned that the Pt/NiHCRu electrode exhibits a rather high rate of self-discharge (Fig. 6). This is, at least in part, due to the oxidation of water, since a smaller pH effects a lower self-discharge rate. A yet stronger lowering of the self-discharge rate of the NiHCRu electrode is achieved when acetonitrile is used as solvent instead of water (Fig. 6).

CONCLUSIONS

From the results obtained it can be concluded that further studies on secondary cells on the basis of nickel

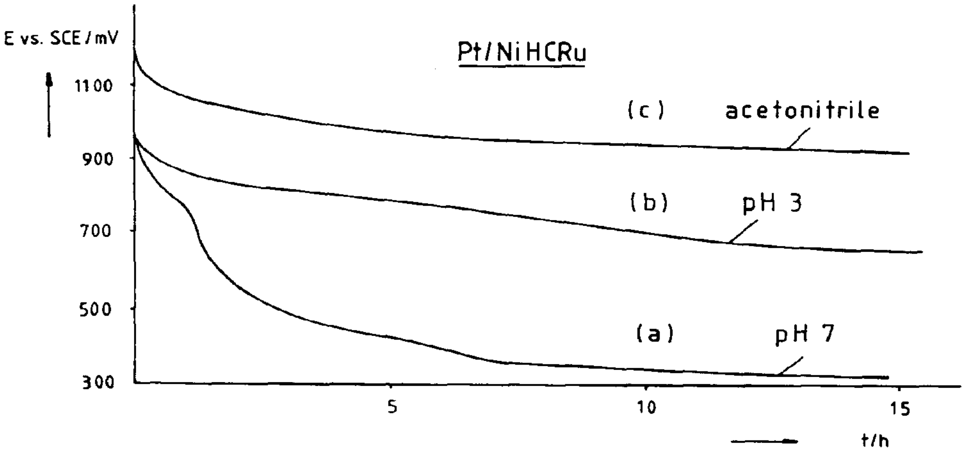


Fig. 6. Open circuit voltage of a Pt/NiHCRu electrode in solutions of 0.1 M $NaClO_4$ in water at pH 7 (a) and pH 3 (b), and in acetonitrile (c).

hexa-cyanometallates should be directed predominantly into two directions: stabilization of the electrodes with respect to self-discharge and enlargement of the charge capacity of the cells.

The first aim can be achieved by using an aprotic solvent (*eg* acetonitrile) instead of an aqueous one. Preliminary experiments show that the NiHCMe electrodes can be reversibly cycled in solutions of sodium perchlorate in acetonitrile, although the waves are broader compared with aqueous solutions. Furthermore, polycarbonate foils metallized with Ni or Pt are proved to be mechanically stable in acetonitrile solutions.

For achievement of the second aim, cells will be built with stacks of metallized foils onto which the NiHCMe films are deposited. The aprotic electrolyte will be fixed between the foils by means of a felt thus leading to a relatively flexible secondary cell.

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REFERENCES

1. W. R. Mc Kinnon and R. R. Haering, in *Modern Aspects of Electrochemistry* (Edited by J. O'M. Bockris and A. Conway, Vol. 15, p. 235 (1983)
2. J. W. Mc Cargar and V. D. Neff, *J. phys. Chem.* **92,** 3598 (1988).
3. K. Itaya, K. Shibayama, H. Akahoshi and S. Toshima, *J. appl. Phys.* **53,** 804 (1982).
4. H. Kellawi and D. R. Rosseinsky, *J. electroanal. Chem.* **131,** 373 (1982).
5. K. Itaya, I. Uchida, S. Toshima and R. M. de la Rue, *J. electrochem. Soc.* **131,** 2086 (1984).
6. A. Viehbeck and D. W. Deberry, *J. electrochem. Soc.* **132,** 1369 (1985).
7. K. Itaya, T. Ataka and S. Toshima, *J. Am. chem. Soc.* **104,** 3751 (1982).
8. S. Sinha, B. D. Humphrey and A. B. Bocarsly, *Inorg. Chem.* **23,** 203 (1984).
9. K. Ogura and S. Yamasaki, *J. chem. Soc. Faraday Trans. I* **81,** 267 (1985).
10. F. Li and S. Dong, *Electrochim. Acta* **32,** 1511 (1987).
11. D. Engel and E. W. Grabner, *Ber. Bunsenges. phys. Chem.* **89,** 982 (1985).
12. E. W. Grabner and D. Engel, *Dechema-Monogr.* **102,** 575 (1986).
13. V. D. Neff, *J. electrochem. Soc.* **132,** 1382 (1985).
14. E. W. Grabner and S. Kalwellis-Mohn, *J. appl. Electrochem.* **17,** 653 (1987).
15. J. Mc Breen, in *Comprehensive Treatise of Electrochemistry*, Vol. 3 (Edited by J. O'M. Bockris, B. E. Conway, E. Yeager and R. E. White), Plenum Press, New York (1981).
16. A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, p. 411, Wiley, New York (1980).