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PAPER

Application of Electrodeposited Cobalt Hexacyanoferrate Film to Extract Energy from Water Salinity Gradients

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Emission of greenhouse gases and limited amount of fossil fuels lead to emerging need for renewable and sustainable energy sources. The Gibbs free energy released when river water flows into the sea can be utilized as a source of energy. Mixing Entropy Battery(MEB) is a novel electrochemical cell which efficiently extracts energy from this natural salinity. It consists of cationic and anionic electrodes. Each of

10 these electrodes interacts selectively with one type of ions. In this work "MEB" principle is applied. The battery is constructed with two inexpensive and easily prepared electrodes including carbon paste electrode modified by cobalt hexacyanoferrate film (CPE-CoHCF) as cathode, and silver/silver chloride as anode. The feasibility of electrochemical oxidation, reduction and cyclic of CoHCF were demonstrated. The AgCl/CPE-CoHCF cell showed the standard cell potential of 0.497 V. The power

15 density of about 24000 $\mu W\ g^{-1}$ with 65% efficiency was achieved with this system, which is a considerable improvement over previous reported results.

1. Introduction

Emission of greenhouse gases and limited amount of fossil fuels lead to emerging need for renewable and sustainable energy

20 sources. Sunlight, wind, geothermal, biomass, and oceans are well known renewable sources of energy, but less well known is salinity gradient. The Gibbs free energy released when river water flows into the sea has been identified as a source of renewable energy.[1] Pressure retarded osmosis (PRO),[2-5] reverse electrodialysis

25 (RED),[4-10] and capacitive mixing (CAPMIX)[11-16] are the most investigated techniques to harvest salinity gradient energy. In PRO, water from a diluted solution flows through a semi-permeable membrane into the pressurized concentrated solution. Depressurizing the transported water can be used to generate

30 electrical power in a turbine.[2-5] In RED, alternating cation and anion exchange membranes separate alternately salt and fresh solutions. The salinity difference on either side of the membrane creates an ion flux, resulting in a potential difference that can be utilized as electrical energy.[4-10] These approaches are membrane

35 based and have some problems such as: membranes high cost, and short life time.[17] In 2009 Brogioli proposed a novel method based on electric double layer (EDL) capacitor technology in which the capacitance of EDL varies with concentration.[12] This pioneering

work, leads to the family of CAPMIX technologies,[13] Capacitive

40 double layer expansion (CDLE),[12] and capacitive donnan potential (CDP),[14] which takes advantages of ion selective membranes and capacitor technology. Another approach is mixing entropy battery (MEB), which has overcome the problems of membranes and the supercapacitor self-discharge.[18] MEB belongs to the accumulator

45 mixing family (AccMix).[19]

Among all the techniques mentioned above, MEB is the youngest. It was proposed by La Mantia et al. in 2011.[18] It consists of two electrodes: anionic electrode, which interacts specifically with Cl^- ions, and cationic electrode, which

50 intercalate/deintercalate Na^+ ions. Energy is produced with a four-step cycle. The battery is charged in fresh solution while the ions exit from their respective electrodes, exchanging the freshwater with saltwater leads the equilibrium potential to increase, then the battery is discharged with entering Na^+ and Cl^- ions into cationic

55 and anionic electrodes, at last exchanging the concentrated solution with diluted one results in the decrease of equilibrium cell potential. With this closed cycle energy is produced.

Few papers about MEB have been published yet.[18-21] In the first work La Mantia et al. obtained the power density of 10.5 μWcm^{-1}

60 with 74% efficiency, and the gained potential was about 0.135V.[18]

In another research in 2013 Jia et al. reported a power density of 1795µWg⁻¹ with 69% efficiency, and $V_G \approx 0.148$ V.[20] Inspired by zinc-silver chloride battery Marino et al. constructed a kind of MEB in which energy was produced with different zinc chloride solutions, the power output of their system was about 2Wm⁻².[19] In the last report, Ye et al. used wastewater effluent for charging of a MEB, the energy recovery for their system was 0.11 kW h per m³ of wastewater effluent.[21]

To further investigates this promising technology, and to study the effect of electrode materials on efficiency and power density, we construct a battery which employs CPE-CoHCF as Na⁺ capturing electrode, and silver sheet as Cl⁻ capturing electrode. Reducing the cost of renewable energy generation is crucial for comparing these recourses with fossil fuels. Nowadays developing new and low cost methods and materials for energy conversion from natural resources has attracted great attention.[22-24] For this reason in the current study we chose CPE-CoHCF because CPEs are easily made and economic, and hexacyanoferrate compounds intercalate and deintercalate alkali metal ions reversibly.[25-31] It is anticipated that with this new cationic electrode higher energy/power density will be produced.

2. Experimental

2.1. Equipment and reagents

Cyclic voltammetry and galvanostatic charge/discharge were performed with SAMA 500 ELECTROANALYZER(Iran). Cyclic voltammetry was accomplished using a three electrode cell, bare or electrochemically modified CPE as working electrode, Ag|AgCl|3MKCl (Metrohm) as a reference electrode and a Pt rod (Metrohm) as a counter electrode. The body of the working electrode was a 5mL polyethylene syringe that was tightly packed with carbon paste. A copper wire inserted into the carbon paste established the electrical contact.CPE-CoHCF was employed as cathode, and silver sheet was used as anode. The geometrical electrodes surface area in contact with the solution was 1.3 cm². The distance between positive and negative electrodes was 1cm.The current of 13 µA was employed for charging and discharging the battery. All the experiments were performed at room temperature.

Potassium hexacyanoferrate, cobalt nitrate hexahydrate, potassium chloride, sodium chloride, graphite fine powder and paraffinoil(Uvasol®) were purchased from Merck and used without further purification. All solutions were prepared with deionized water. The electrolyte solutions were 0.6M NaCl as artificial sea water and 0.024M as artificial river water (other concentrations of NaCl between 1 – 200mM were also used).

The morphology of the electrode surface was examined by scanning tunneling microscope model of Nanoscope® II in AFM mode. The analysis of the AFM images were done by Nanoscope III 5.12r2 software.

2.2. Preparation of cationic electrode

CPE was prepared by mixing the graphite powder with paraffin oil (70:30) to obtain a uniform paste. This paste was housed in a polyethylene syringe (area = 1.3cm²), and then polished with a weighing paper. CoHCF films were electrodeposited on CPE with repetitive cyclic voltammetry from 0.0 to +1.1 V at100mV s⁻¹,[32] from a fresh solution mixture containing 0.5 M KCl, 1mM

Co(NO₃)₂, and 0.5 mM K₃Fe(CN)₆. After 72 cycles, modified electrode was taken out and rinsed thoroughly with water. It is important that this mixed solution should be prepared freshly and for obtaining reproducible result it is better to mix them in similar steps.[33] In the current study solutions were added according to this order: KCl, K₃Fe(CN)₆ and Co(NO₃)₂.

3. Results and Discussions

3.1. Electrochemical properties of CPE-CoHCF

Fig. 1 illustrates the cyclic voltammogram (CV) during the electrodeposition process. The gradual increase in currents for both cathodic and anodic peaks shows that CoHCF films were formed on the electrode surface, and its thickness grows progressively. Finally a limiting contour of the cyclic voltammogram is obtained (71ᵗʰ and 72ⁿᵈ cycles are identical).
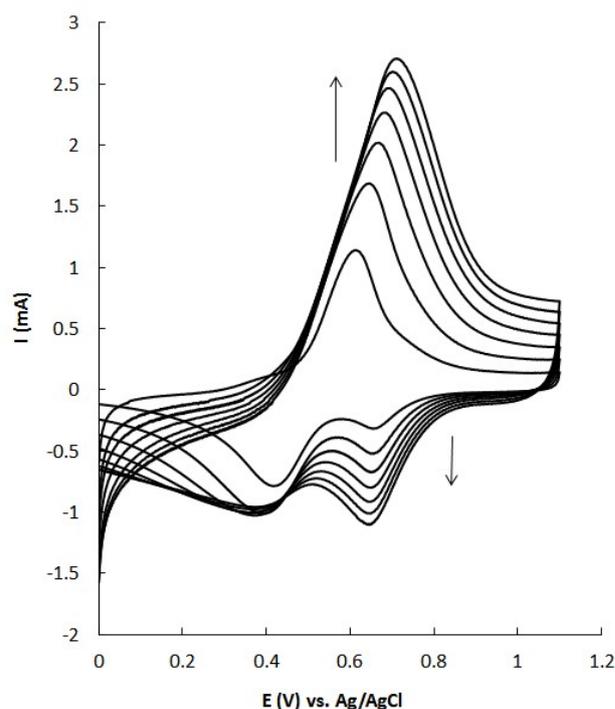
Fig. 1.CVs for electrodeposition process of CoHCF film on CPE. The 10, 20, 30, 40, 50, 60 and 72ⁿᵈ cycles are illustrated.

The morphology of electrodeposited CoHCF film was studied with AFM. The results of surface morphology studies show that formation of hexacyanoferrate on the carbon particles make an almost uniform nanometric roughness on the electrode surface (the roughness value is about 130 nm) (see Fig. 2).

Typical CV of CPE-CoHCF obtained in 0.6 and 0.024 M NaCl solutions at scan rate (*v*) of 100 mV s⁻¹ between 0 and +1.1 V is shown in Fig. 3. This figure demonstrates that the position and height of the redox peaks depends on the solution concentration. In 0.6 M solution two pairs of reversible redox peaks can be observed and the formal potentials ($E° = (E_{p,a} + E_{p,c})/2$) are about 0.48 and 0.88 V respectively. The two sets of redox peaks were explained as the existence of two possible forms of CoHCF,

These equations demonstrate that reduction and oxidation of CoHCF take place with intercalation and deintercalation of Na^+ ions.

The CPE-CoHCF was studied in 0.6M NaCl solution by cyclic voltammetry at different v over a range of $10 - 100mVs^{-1}$ between 0 and +1.1V. Plotting the peak currents (I_p) against v obtains straight lines for both anodic and cathodic reactions, indicating the adsorption process of modified electrode (Fig. 4).

The peak to peak potential separation is about 85 mV for v of 10 mVs^{-1}. The formal potential is approximately independent of the v which represents facile charge transfer kinetics. The surface coverage (Γ) can be calculated from the equation $\Gamma = Q/nFA$, here Q is the charge obtained by integrating the first anodic peak under the background correction (at a low v of 10 mVs^{-1}), F is Faraday constant, A is electrode area and n is the number of electrons. In the present study, by assuming the involvement of one electron in the process, the calculated value of surface coverage is 6.43×10^{-8} molcm^{-2}, which means that the active material deposited on the electrode is about 19.3µg cm^{-2}.

Fig. 2. AFM images of CoHCF film on carbon paste.

$NaCo^{II}_{1.5}Fe^{II}(CN)_6$ and $Na_2Co^{II}Fe^{II}(CN)_6$, and have been attributed to the transformations between Fe(II) and Fe(III) in $NaCo^{II}_{1.5}Fe^{II}(CN)_6$ and $Na_2Co^{II}Fe^{II}(CN)_6$, respectively.[32] According to previous reports the redox reaction of Na^+ can be expressed as follows:[34,35]

$$Co^{(II)}_{1.5}[Fe^{(III)}(CN)_6] + e^{-1} + Na^+ \rightleftharpoons NaCo^{(II)}_{1.5}[Fe^{(II)}(CN)_6] \quad (1)$$

$$NaCo^{(II)}[Fe^{(III)}(CN)_6] + e^{-1} + Na^+ \rightleftharpoons Na_2Co^{(II)}[Fe^{(II)}(CN)_6] \quad (2)$$
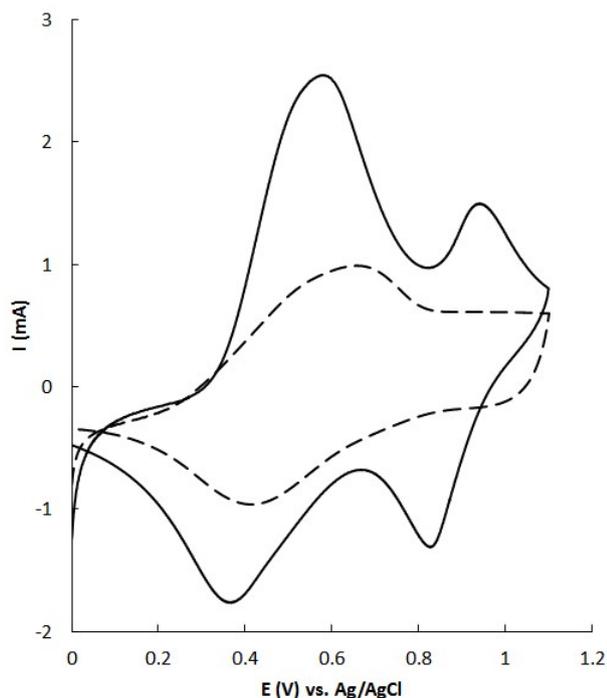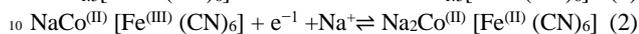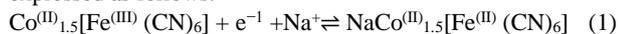
Fig. 3. CV of CPE-CoHCF in 0.6 (solid line) and 0.024M NaCl solution (dashed line) (v= 100 mVs^{-1})

Fig.4. CVs of CPE-CoHCF in 0.6 M NaClsolution at various $v$over the range of 10-100 mVs^{-1}. Inset:Plot of anodic and cathodic peak currents of the first redox couple of CoHCF against$v$.

The stability of CPE-CoHCF was examined with cyclic voltammetry, after 100 cycles with v = 100 mVs^{-1} of consecutive scanning in 0.6 M NaCl solution there is about 20% decrease in the first peak current for the first redox couples.

3.2. Electrochemical thermodynamics of the cell

As assembled, the AgCl/CPE-CoHCF cell showed an open circuit potential of about 300 mV. To avoid contamination with K^+ ions, the cell was first charged in 0.024M NaCl solution until the potential reach to 1.2V. After washing the electrodes with water and exchanging the solution with fresh one the cell discharged to 0.2V.

In this experiment potentials do not exceed 600mV after charging, so we assume the half reactions as follows:

$$Co^{(II)}_{1.5}Fe^{(III)}(CN)_6+e^-+Na^+ \rightleftharpoons NaCo^{(II)}_{1.5}Fe^{(II)}(CN)_6 \quad (3)$$

$$AgCl+ e^- \rightleftharpoons Ag+ Cl^- \quad (4)$$

The overall reaction is:

$$Co^{(II)}_{1.5}Fe^{(III)}(CN)_6+ Ag + NaCl \rightleftharpoons NaCo^{(II)}_{1.5}Fe^{(II)}(CN)_6 + AgCl (5)$$
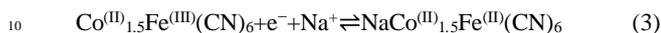
The potential difference between the two electrodes is:

$$E_{Cell}= E^0_{Cell}+ 2\frac{RT}{F}ln\ (C_{NaCl}) +2\frac{RT}{F}ln\ (\gamma_{NaCl}) \quad (6)$$

Where E^0_{Cell} is the standard cell voltage, C_{NaCl} the concentration of NaCl, and γ_{NaCl} the mean activity coefficient of NaCl. Equation 6 can be rearranged as:

$$E_{Cell}- 2\frac{RT}{F}ln(C_{NaCl})=E^0_{Cell}+2\frac{RT}{F}ln\ (\gamma_{NaCl}) \quad (7)$$

E_{Cell} or open circuit potential (OCP) may be measured in various concentration of NaCl solution. Fig 5. Shows the equilibrium cell potentials for different NaCl concentrations.
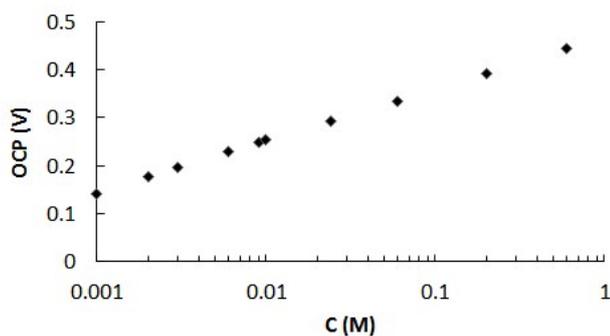
Fig.5.OCPs for AgCl/CPE-CoHCF in different concentrations of NaCl solutions.
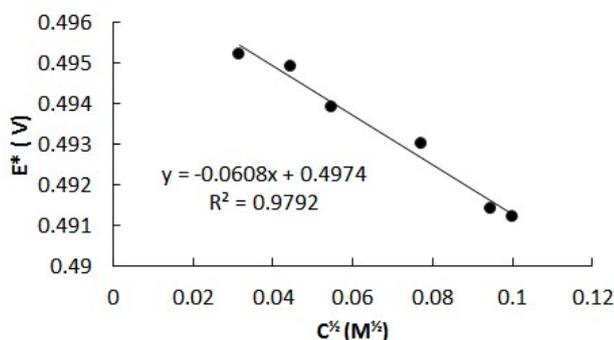
Fig.6.plot of E* against c$^{1/2}$ for 1-10 mM NaCl solution.
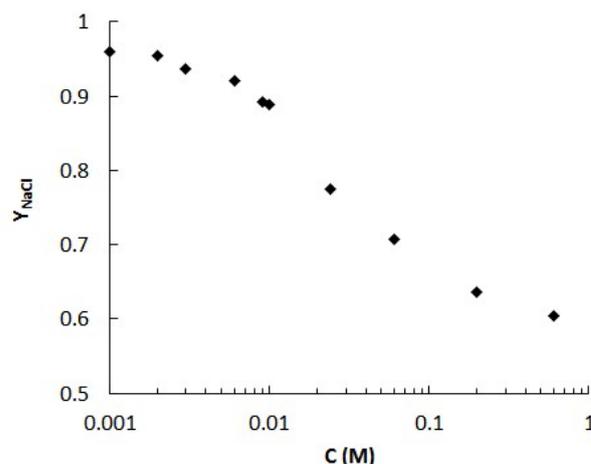
Fig.7. Mean activity coefficient of NaCl solution at different concentrations.

By plotting the left-hand side of the equation 7 (E*) vs. $C^{1/2}$, in the range of values where Deby-Hückel limiting law holds, E^0_{Cell} will be found by extrapolation.[36,37] The concentration range from 1 – 10mM were fitted to this equation (Fig.6).

As demonstrated in Fig 6. the standard cell potential is gained 0.497 V, and the value of A, in the Deby-Hückel limiting law ($ln\gamma_{NaCl}$= -2.303 $AC^{1/2}$)is obtained about 0.51 $M^{-1/2}$, which is in good agreement with the theoretical prediction (0.5115$M^{-1/2}$) [37].

Using the values calculated for E_{Cell}, the mean activity coefficients can be found. The values of γ_{NaCl} at different concentrations from 1 to 600 mM is illustrated in Fig.7.

The thermodynamic gained potential (V_G) is defined as the difference in equilibrium cell potential in concentrated and diluted solution.[18] In current study V_G~ 0.153 V was measured, which is higher than previous reports.[18,20]
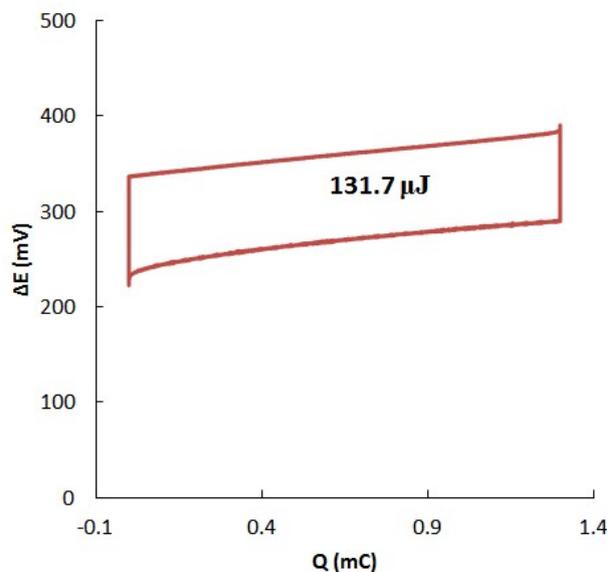
Fig.8. First cycle of energy extraction for AgCl/CPE-CoHCF system.

Values for mean activity coefficients are applied to calculate the Gibbs free energy of mixing. If a volume V_D of a diluted NaCl solution combines with a volume V_C of concentrated one to give a volume V_B of brackish solution ,the total amount of Gibbs free energy per unit volume of brackish solution is determined by (for example see ref 38):

$$\Delta G_{mix}=2RT[C_B\ln(\gamma_B C_B) - \varphi C_C \ln(\gamma_C C_C) - (1-\varphi)\, C_D \ln(\gamma_D C_D)] \quad (8)$$

Where φ is volumetric ratio of concentrated solution to the total system volume, and other symbols have their usual meanings. In the present study the error committed by assuming the solutions to be ideal is about 40 Jdm^{-3} which is 4.7% of the total Gibbs free energy (850 Jdm^{-3}).

3.3.   Cycles of energy extraction

A four step cycle performed as follows:

First step: The battery was charged in 0.024M NaCl solution with the current of 13μA and time limit of 100 s.

Second step: The diluted solution was exchanged for concentrated one (0.6M NaCl), the equilibrium potential is measured for 10 s. The potential rise is about 100 mV.

Third step: The battery was discharged by applying -13μA current for 100 s.

Fourth step: The concentrated solution was substituted by diluted one, and the OCP was measured within 10 s.

In Fig. 8. the first energy extraction cycle for AgCl/CPE-CoHCF has been shown. The battery generates   131.7 μJ in the first cycle which equals to the energy density of 5249 mJ g^{-1}. To calculate the power density, the energy density must be divided by time spend for energy extraction, since 220 seconds have been spent for the extraction of energy the power density gained is about 24000 μWg^{-1}, which is significantly higher than previous MEB devices that have been studied in 0.024 M and 0.6 M NaCl solutions.[18,20] The energy efficiency for this system is about 65%, and with this new cationic electrode the highest gained potential was observed (V$_G$= 152.6 mV).

Fig.9. illustrates the values of extracted energy versus the number of cycle. It can be seen that the system shows a little loss in energy production.

To obtain more power, higher current densities must be applied, so the higher quantities of active material is necessary.[20] Since with this procedure not more than μg of active material can be electrodeposited, our future work will focus on constructing electrodes with nanoparticles of CoHCF on carbon cloth.
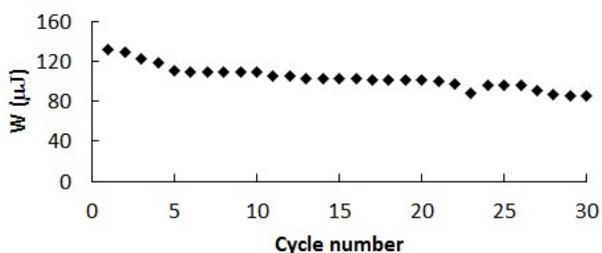
Fig.9. Energy extracted vs. number of cycle for AgCl/ CPE-CoHCFbattery.

4.   Conclusions

A thin film cathode for the mixing entropy battery has been prepared using repetitive cyclic voltammetry, and characterized with electrochemical techniques. The battery constructed with AgCl/CPE-CoHCF with standard cell potential of 0.497 V, was used to extract salinity gradient energy. The power density gained, which is very better than the recent reports, was about 24000 μW g^{-1} with 65% efficiency. In this study the preparation procedure of the cationic electrode was easy and economical and the materials were environment friendly. We believe that the mixing entropy battery is a powerful device to efficiently extract energy from differences in salinity. Further investigations are necessary to improve this promising technology.

Notes and references

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