

## Water-Miscible Room-Temperature Ionic Liquid-Cobalt Hexacyanoferrate Gel Modified Electrode for Electrocatalytic Oxidation of NADH

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Cobalt hexacyanoferrate particles were ground with water-miscible room-temperature ionic liquid, 1-methylimidazolium trifluoroacetic acidic salts (HMImTfa), and resulted in HMImTfa-CoHCF gel. The electrochemical properties of HMImTfa-CoHCF gel were investigated in detail. The impedance data show that HMImTfa-CoHCF gel is mixed ionic-electronic and has 2.5 times the improvement of the conductivity than that of pure HMImTfa. HMImTfa-CoHCF gel can be used in chemically modified electrode for the electrocatalytic oxidation of NADH. The corresponding results have important implications for the design of nano-structured and nano-composite materials based on water-miscible room-temperature ionic liquids, which could be used widely in chemo/biosensing and catalysis.

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**Keywords:** Cobalt hexacyanoferrate, ionic liquid, electrocatalysis, NADH

### 1. INTRODUCTION

Room-temperature Ionic liquids (RTILs) are ionic media resulting from the combination of organic cations and various anions. They are liquids at room temperature and represent a new class of nonaqueous but polar solvents that are able to dissolve many compounds [1]. RTILs have attracted considerable attention in the past because of their unique chemical and physical properties, such as

high chemical and thermal stability, negligible vapor pressure and high conductivity [2-3]. The RTILs have been used in various research fields including organic synthesis, catalysis and extraction. Moreover, many attempts have revealed that the RTILs are advantageous over other kinds of solvents for electrochemical studies and applications [4-7].

The investigations of the electrochemical properties and applications of the RTILs have been generally conducted either by using the RTILs as solvent for electrochemical measurements without the addition of an external supporting electrolyte or by confining IL droplets to solid substrates to form supported liquid phases (SLPs) with different thicknesses. The former method has been widely used in the past for solution voltammetry and metal electrodeposition particularly. The latter has recently been developed for electrochemical investigations. However, the strategies for confining RTILs on solid substrates through the formation of SLPs are limited only for the RTILs that are immiscible with water, and only few papers concern about the use of water-miscible RTILs on solid substrates for the electrochemical application [8].

On the other hand, transition metal hexacyanoferrates (MHCFs) belong to a group of excellent electron-transfer mediators that have attracted great attention [9-10]. The modification of electrode surface with MHCFs has led to the development of various electrochemical sensors. Among the metal hexacyanoferrates, cobalt hexacyanoferrate (CoHCF) would appear to be especially attractive because of its interesting chemical and electrochemical properties [11-13]. CoHCF exhibits not only electrocatalytic or mediator activities via slow electrochemical reactions but also ion selectivity, the ability to store cations, electrochromic, thermochromic characteristics, solid-state batteries and molecular magnetism.

In this paper, water-miscible RTIL was used as a matrix to entrap CoHCF. The properties of the resulting RTIL-CoHCF gel were investigated by ac impedance. The RTIL-CoHCF gel is mixed ionic-electrical and almost 2.5 times the improvement of the conductivity than that of pure RTIL. The as-prepared RTIL-CoHCF modified electrode provides a useful avenue for electrochemical applications of water-miscible RTIL, such as the electrocatalytic oxidation of NADH.

## 2. EXPERIMENTAL

### 2.1. Reagents and apparatus

Water-miscible RTIL used in this study is 1-methylimidazolium trifluoroacetic acidic salts (HMIImTfa). NADH (in the form of sodium salt, >92% purity) was purchased from Shanghai Lizhu Dongfeng Biotechnology Co. Ltd., China. All other chemicals were analytical grade. Double-distilled water was used throughout.

Cyclic voltammetry measures were carried out in a conventional three-electrode cell controlled by CHI 660D Electrochemical Work Station (CH Instruments, Inc). Pyrolytic graphite (PG) electrode (surface area 0.06 cm<sup>2</sup>) was used as working electrode. A platinum foil was applied as the counter electrode and a saturated calomel electrode (SCE) served as reference electrode. All potential values given below refer to SCE. All experiments were performed at room temperature.

Electrochemical impedance measurements were carried out with an Advanced Electrochemical System (PARSTAT 2273, Princeton Applied Research, USA) in Faraday cage at ambient temperature. The samples were sandwiched by two parallel blocking platinum electrodes into a sealed glass cell. The area and distance between the two Pt electrodes are  $0.09 \text{ cm}^2$  and  $0.5 \text{ cm}$ , respectively. The conductivity was determined by ac impedance in the frequency range between  $0.01 \text{ Hz}$  to  $100000 \text{ Hz}$  with signal amplitude of  $5 \text{ mV}$ .

The morphology and elemental composition of the modified electrodes were characterized by scanning electron microscopy (SEM, JSM 5600LV, operating at  $20 \text{ kV}$ ) and energy dispersive X-ray spectroscopy (EDS, Vantage 4105, NORAN).

## 2.2. Preparation of CoHCF particles

CoHCF particles were synthesized by addition of  $25 \text{ mL}$  of a  $10 \text{ mM}$  aqueous solution of  $\text{CoCl}_2$  dropwise to a  $25 \text{ mL}$   $0.1 \text{ M}$  KCl solution containing  $20 \text{ mM}$   $\text{K}_3\text{Fe}(\text{CN})_6$  under vigorous stirring. After complete addition, the mixture was stirred continuously for an hour. The precipitates were centrifuged three times and washed each time with double distilled water to remove the excessive potassium ions and chloride ions. Finally, brown products were obtained by dried overnight in a vacuum.

## 2.3. Preparation of HMImTfa-CoHCF modified electrode

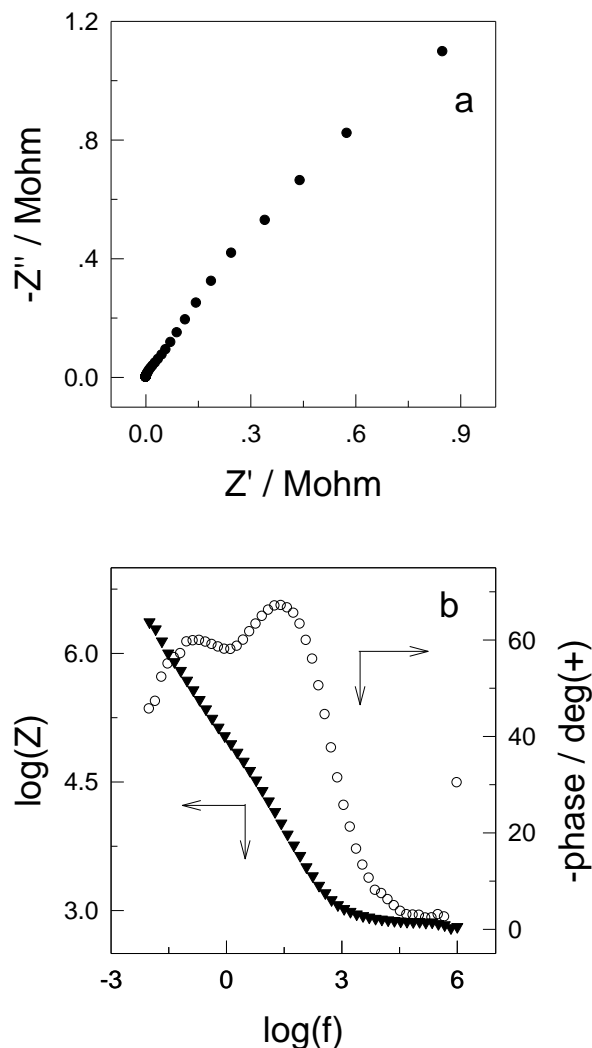
First,  $2 \text{ mg}$  CoHCF particles mixed with  $5 \mu\text{L}$  pure HMImTfa were ground with an agate mortar for about  $30 \text{ min}$ , and a brown gel was formed, which is similar to the black IL-CNT gel [14]. Meanwhile, the pyrolytic graphite (PG) electrode (surface area  $0.06 \text{ cm}^2$ ) was polished with alumina, followed with being washed in double-distilled water and ethanol, respectively, and activated in  $0.5 \text{ M}$  sulfuric acid. Then, the PG electrode was rubbed over the CoHCF gel placed on a smooth glass slide for almost  $15 \text{ min}$ , and the gel was mechanically attached to the electrode surface. After the gel on the electrode surface was smoothed with a spatula to leave a thin gel film on the PG electrode surface. Finally,  $0.5 \text{ wt}\%$  Nafion solution was cast on the surface of the resulting electrode.

# 3. RESULTS AND DISCUSSION

## 3.1. Electrochemical properties of HMImTfa-CoHCF gel

The Nyquist and Bode plot of pure HMImTfa were illustrated in Fig.1. From Nyquist plot, the spectrum for the sample sandwiched with blocking platinum electrodes shows a quasi-straight line indicating that an ion diffusion process plays the major role and there is no ion insertion reaction at the Pt/IL interface [4]. From Bode plot, in the high-frequency region ( $10^6$ - $10^3 \text{ Hz}$ ), the impedance curve is almost quasi-independent of frequency and the phase angle value approaches 0. This is a typical response for a resistive behavior, which corresponds to a resistance of the sample sandwiched by the two parallel electrodes. The electrolyte solution resistance ( $R_\Omega$ ) is calculated and equals to  $812.8 \Omega$ . In

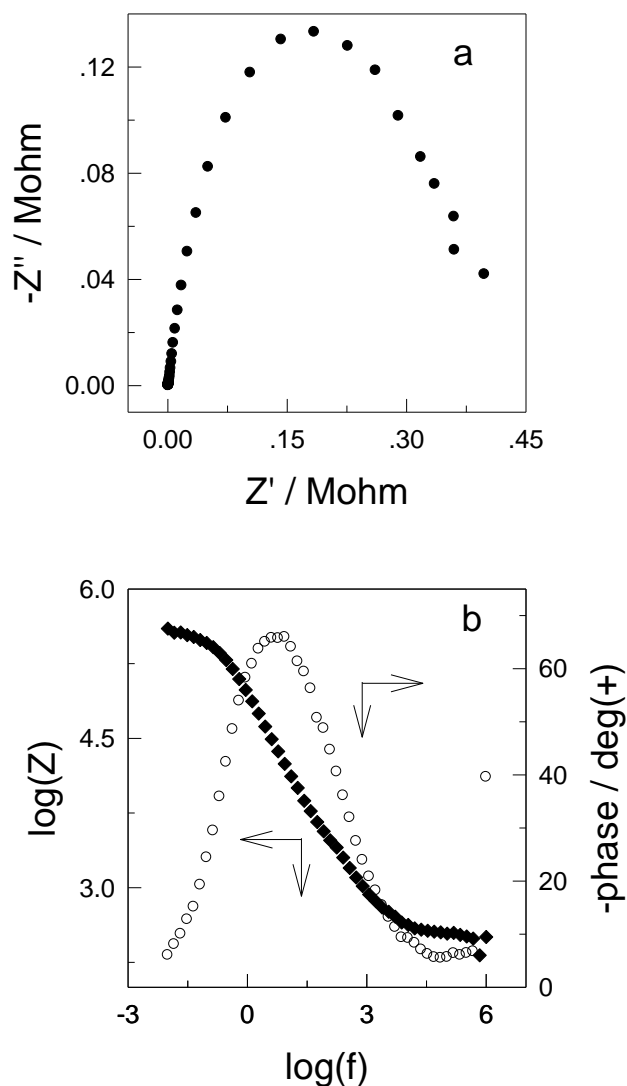
other frequencies regions, a linear relationship can be observed between the module  $Z$  and the frequency with a slope of about  $-0.7$  for pure HMIImTfa. This frequency range corresponds to a capacitive behavior of the Pt/IL interface [15]. Additionally, the minimum phase angle is  $-67.1^\circ$  at around 26.8 Hz.



**Figure 1.** Nyquist plot (a) and Bode plot (b) of pure HMIImTfa at ambient temperature. The frequency range is from  $10^6$  to  $10^{-2}$  Hz, and the signal amplitude is 5 mV.

Fig.2a presents the Nyquist plot of HMIImTfa-CoHCF, which is obviously different from that of pure HMIImTfa. An obvious semicircle can be observed, which corresponding to the electron-transfer-limited process. From Bode plot (Fig. 2b), the minimum phase angle is  $-65.9^\circ$  at around 8.7 Hz and the slope between the module  $Z$  and the frequency is  $-0.6$ . The smaller the slope value, the weaker the pure capacitive behavior.  $R_\Omega$  is calculated and equals to  $338.8 \Omega$ . From ac impedance technology, the conductivity of HMIImTfa-CoHCF is mixed ionic-electrical, and there is almost 2.5 times the improvement of the conductivity than that of pure HMIImTfa. These imply the addition of

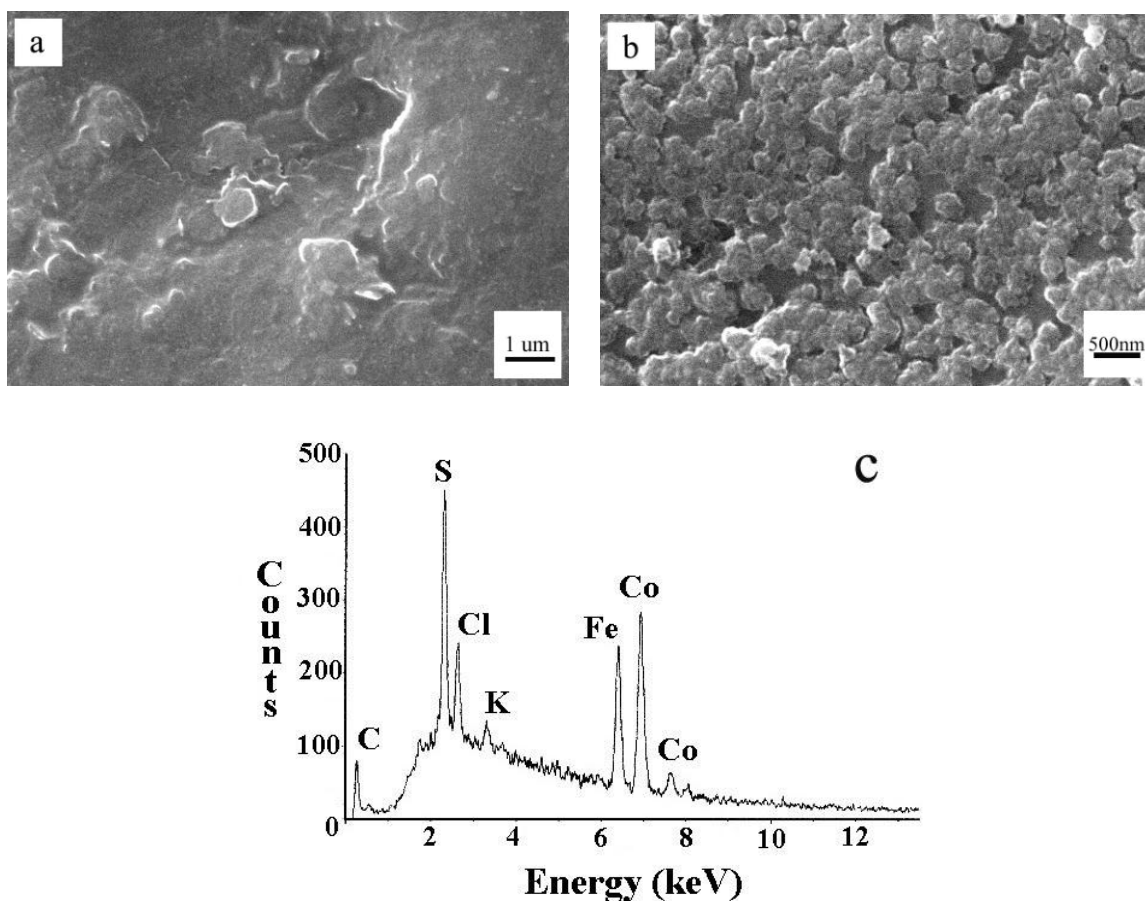
CoHCF particles can promote the electron-transfer reactions in the system due to the excellent electrical properties of CoHCF.



**Figure 2.** Nyquist plot (a) and Bode plot (b) of HMImTfa-CoHCF at ambient temperature. The frequency range is from  $10^6$  to  $10^{-2}$  Hz, and the signal amplitude is 5 mV.

The various micrographs of PG/HMImTfa and PG/HMImTfa-CoHCF electrodes were shown in Fig. 3. From Fig. 3a, a compact film of HMImTfa was covered on carbon layer. In Fig. 3b, it can be observed that uniform CoHCF particles with diameter of 200-300 nm were embedded in HMImTfa film and resulting in the three-dimensional structure. The presence of CoHCF is also confirmed by EDS investigation. From Fig. 3c, C, S, Cl, K, Fe and Co are the major elements. The existence of Fe and Co element indicates that CoHCF exists actually on the matrix of HMImTfa film. HMImTfa may act as ion carriers to transport charges between CoHCF particles. Thus, the conductive performance of the HMImTfa-CoHCF was notably improved due to the matrix ionic (HMImTfa) and electronic

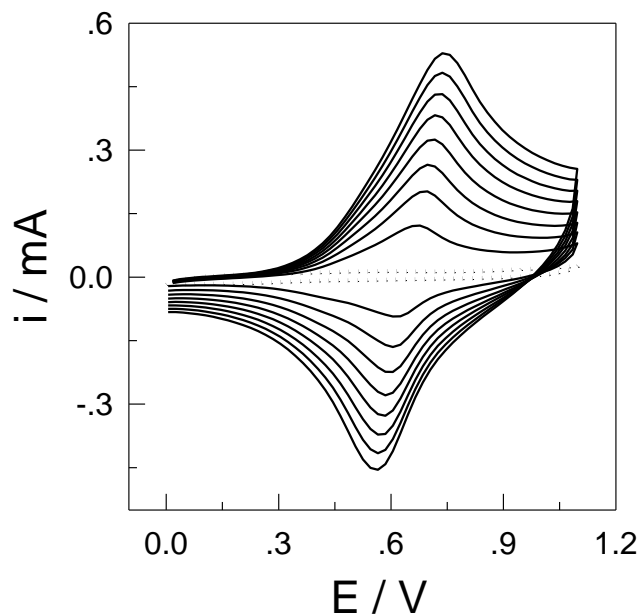
(CoHCF) contribution. Moreover, this kind of character may be potentially used in catalytic, modified electrode, biosensor, electronic, optical, and magnetic fields.



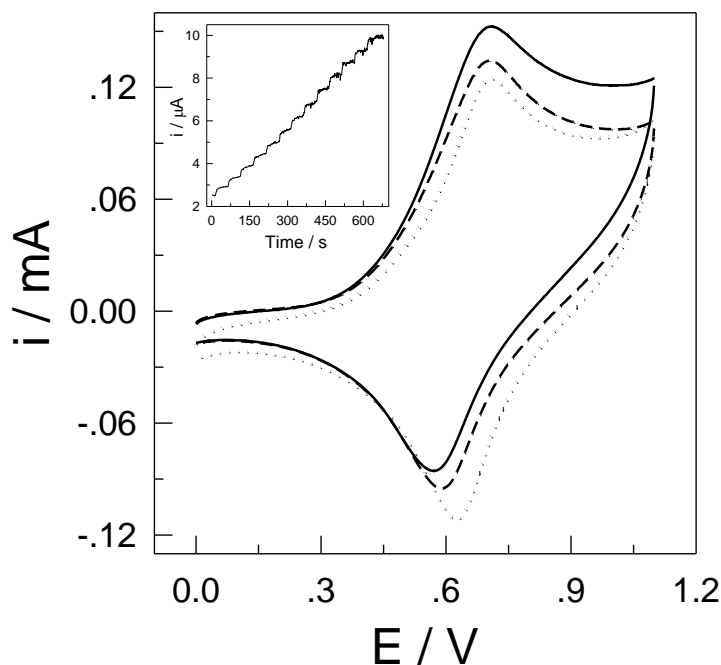
**Figure 3.** (a) SEM image of HMImTfa modified PG electrode, (b) and (c) SEM and EDS pattern of HMImTfa-CoHCF modified PG electrode.

### 3.2. Preliminary application of HMImTfa-CoHCF modified PG electrode

Fig. 4 shows cyclic voltammograms of PG/HMImTfa-CoHCF electrode in 0.07 M PBS solution (pH 7.0) with different scan rate. One reversible redox peaks of CoHCF can be observed. Due to the mixed ionic-electronic property of HMImTfa-CoHCF, the current at PG/HMImTfa-CoHCF electrode is larger than that at the bare PG electrode at the same scan rate. The formal potentials of the redox peak,  $E_{1/2}$  ( $E_{1/2} = E_{Pa}/2 + E_{Pc}/2$ ), is at + 0.64V, which have been attributed to the transformations between Fe(II) and Fe(III) in  $KCo^{II}[Fe^{III}(CN)_6]$ . Therefore, redox couple can be expected as  $KCo^{II}[Fe^{III}(CN)_6]/K_2Co^{II}[Fe^{II}(CN)_6]$  [16]. Additionally, all the peak potentials slightly change while the anodic and cathodic peak currents increased linearly with the increase of scan rate. This reveals that the electrochemical behavior of CoHCF in HMImTfa matrix on the surface of PG electrode shows a surface confined redox process.

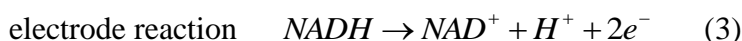
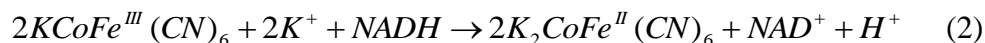


**Figure 4.** Cyclic voltammograms of the PG/HMImTfa-CoHCF electrode (solid line) in a 0.5 M  $\text{H}_2\text{SO}_4$  solution at different scan rates: 50, 100, 150, 200, 250, 300, 350, 400  $\text{mV s}^{-1}$  (from inside to outside). Dotted line represents the cyclic voltammograms of bare PG electrode in same solution at 50  $\text{mV s}^{-1}$ .



**Figure 5.** Cyclic voltammograms of PG/HMImTfa-CoHCF electrode in 0.07 M phosphate buffer solution (pH 7.0) without (dotted line) and with 3 mM (dashed line) and 10 mM (solid line) NADH. The inset is the current-response time of the PG/HMImTfa-CoHCF electrode to addition of 0.1 mM NADH at 0.65 V in 0.07 M phosphate buffer solution (pH 7.0).

The cyclic voltammograms of the HMIImTfa-CoHCF modified electrode in 0.07 M PBS solution (pH 7.0) containing NADH were shown in Fig.5. It can be seen that, compared to the voltammogram without NADH, the increase of the anodic peak and the decrease of the cathodic peak, which correspond to the reduction of hexacyanoferrate(III) to hexacyanoferrate(II) by NADH. The overall process according to the electrochemical catalytic mechanism can be expressed as [17]:



Additionally, the typical current-time curve for consecutive addition of 0.1 mM NADH was carried out. The response current is linear with NADH concentration up to 1.3 mM with the coefficient of 0.997.

#### 4. CONCLUSIONS

We have demonstrated the simplicity and effectiveness of formation of HMIImTfa-CoHCF gel, in which water-miscible HMIImTfa was used as a physical trigger for CoHCF network. The ac impedance technology was carried out and the corresponding results show that HMIImTfa-CoHCF composite has the better conductivity. This gel material has been succeeded in electrocatalytic oxidation of NADH. This demonstration paves a new way to study the possible applications of water-miscible RTILs in aqueous solution.

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