FT-IR in situ thermoelectrochemical cell for electrode kinetics study

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Abstract. The main parameter, that determines the use of thermoelectrochemical converters (TECC) for the waste heat harvesting is the efficiency of thermoelectric conversion. An increase of the current density at the electrode is possible due to the use of heterogeneous redox catalysts. In this paper, early results of Ti-based mineral catalysts usage are presented. A new type of thermoelectrochemical cell for in situ FTIR spectroscopy was designed, assembled and tested. With its use, the pattern of the redox reaction in $K_3[Fe(CN)_6] \leftrightarrow K_4[Fe(CN)_6]$ conversion was confirmed.

1. Introduction

Low-temperature heat sources (T\textless=100°C) are a huge energy resource, due to their widespread distribution. These include scattered heat of various technological processes, heat fluxes emitted by utilities, the heat of the human body, or the infrared spectrum of sunlight. The use of low-temperature heat will significantly reduce the cost of power supply facilities in remote regions. For example, they can be used for power supply of wireless sensors and transmission of short signals [1]. However, the collection and conversion of low temperature heat is a complex technical problem. An important parameter of thermoelectric converters is the conversion efficiency. At the moment, the efficiency of such converters can reach 3%. According to some estimates [2] the efficiency required for use of this type of electric power sources is estimated at 5%.

Recently, a lot of research has been devoted to improving the efficiency of thermoelectric conversion by modifying the electrolyte [3,4] and electrodes [5,6]. Besides the main electrode material to increase the thermoelectric conversion efficiency perspective to use a modifier, for example, substances with catalytic activity. Another important task is a detailed study of the processes occurring on the electrodes in thermoelectrochemical cells. Knowledge of the transformations of substances in the processes of sorption and charge transfer will help the correct choice of catalyst materials for the oxidation and reduction processes.

A strong and accurate tool for obtaining a detailed description of the electrode surface properties is the use of a probe molecule in combination with a research method that is able to control the
interaction of the probe and surface with sufficient accuracy. Fourier transfer Infrared spectroscopy (4200–400 cm⁻¹) corresponds to this method - it uses the appropriate probe molecules.

2. Ti-based materials in TECC

The most common Ti-based mineral material is TiO₂. In early research, titanium dioxide was used as a modifier of electrode material. Nanoparticles of rutile TiO₂ were infiltrated in carbon fiber «Busofit». TECC was assembled in stainless steel case Coin Cell CR 2025. Using method of impedance spectroscopy with thermostating cell from 25°C to 75°C by step 10°C values of electrode process resistance were obtained. Using Arrhenius equation activation energy values of electrode-electrolyte charge transfer were calculated and represented on figure 1.

The other group of Ti-based mineral material with photocatalytic activity are various potassium titanates – pure and doped with other metals. The most promising material in TECC is $K_{1.4}Ti_{6.6}^4Ti_{1.4}^{3+}O_{16}$ potassium titanate with hollandite structure. Cell was assembled in stainless steel case Coin Cell CR 2025 with $K_{1.4}Ti_{6.6}^4Ti_{1.4}^{3+}O_{16}$ as a bulk thermal separator with catalytic properties. It was added in 0.3 mole/l $K_3[Fe(CN)]_6 / K_4[Fe(CN)]_6$ electrolyte with 1:1 ratio. The comparison was made with system without any thermal separator by impedance spectroscopy using an Arrhenius equation. Results are represented on figure 2.

![Arrhenius plot](image1.png)

Figure 1. Arrhenius plot (a) and values of activation energy (b) for TECC with titanium dioxide as electrode modifier with catalytic properties.

![Arrhenius plot](image2.png)

Figure 2. Arrhenius plot (a) and values of activation energy (b) for TECC with $K_{1.4}Ti_{6.6}^4Ti_{1.4}^{3+}O_{16}$ potassium titanate with hollandite structure as bulk thermal separator with catalytic properties.
3. FT-IR in situ TECC

For studying the course of electrode reactions with catalysts by Fourier-transform infrared spectroscopy a specific thermoelectrochemical cell was designed. It is schematically shown on figure 3. It includes two titanium conductors of heat and current (1), IR spectrometer window of ZnSe with flat transmission spectrum (2) and electrolyte channel by analogy with salt bridge in classic electrochemical cell (3).

![Figure 3. Scheme of cell for FTIR in situ spectroscopy.](image)

The body of cell was made of acrylic glass 6 mm thick for top plate and 3 mm thick for bottom plate. After production of the cell some improvements were made - rubber sealant and fasteners were installed.

4. Experimental

A simple but indicative experiment was carried out with a minimum number of different materials in the cell. At first, probe substances whose spectra are unique and clearly visible during measurements were determined.

The probe substances and their characteristic absorption frequencies were determined as follows: a spectrum of a cell filled with distilled water and electrolyte was obtained (figure 4). The spectrum of the cell with water was obtained with the air as the reference spectrum to determine the intrinsic spectrum of the cell; the spectrum of the cell with the electrolyte was obtained with the water as the reference spectrum (figure 4).

Spectrum analysis of the cell with water indicated, that the absorption peaks at 1640 cm\(^{-1}\), 1540 cm\(^{-1}\), 1240 cm\(^{-1}\), 2920 cm\(^{-1}\) and 2850 cm\(^{-1}\) refer to the polymer compounds of the cell body [7], the absorption peak of 2350 cm\(^{-1}\) refers to carbon dioxide. The presence of an electrolyte based on K\(_3\)[Fe(CN)\(_6\)] and K\(_4\)[Fe(CN)\(_6\)] causes the appearance of absorption peaks at 2110 and 2040 cm\(^{-1}\), which arise due to stretching vibrations of the C–N bond in cyanoferate and cyanoferrite ions [8].
For the experiment, the thermoelectrochemical IR in situ cell was filled with K₄[Fe(CN)₆] solution, the counter electrode was actively cooled, and the electrodes were closed to reduce the resistance to the electrode process due to the potential on the electrode. The resulting spectrum and the spectra of cells with an electrolyte based on K₃[Fe(CN)₆] and K₄[Fe(CN)₆] separately are represented on figure 5.

For the redox reaction in a thermoelectrochemical cell based on potassium ferrocyanide and potassium ferricyanide only one type of ions is sufficient. In presence of only [Fe(CN)₆]⁴⁻ ions and a temperature difference on a surface of the hot electrode the reaction proceeds in accordance with:

\[ Fe(CN)_6^{4-} - e^- = Fe(CN)_6^{3-} \]  \hspace{1cm} (1)

\[ Fe^{2+} - e^- = Fe^{3+} - 74.39 \frac{k}{\text{mole}} \]  \hspace{1cm} (2)

According to the results of spectroscopy, an oxidation reaction proceeds on the hot electrode, the [Fe(CN)₆]⁴⁻ ion gives off the electron and becomes the [Fe(CN)₆]³⁻ ion, which is reflected by the separating the absorption peak 2110 cm⁻¹ of the peak of 2040 cm⁻¹.

Figure 4. Absorbance spectrum of cell, filled with distilled water (top) and absorbance stectrum of electrolyte in cell (bottom).

Figure 5. Absorption spectra of cells with K₃[Fe(CN)₆] (bottom), K₄[Fe(CN)₆] (middle) and cells with K₄[Fe(CN)₆] (top) under forced cooling to create a temperature difference.
The cell performance was confirmed by the I–V curve with the temperature difference on the electrodes about 10°C. The dependences of the current strength and the specific power of the cell are shown in figure 6.

Figure 6. I-V curve and P-V curve of FT-IR in situ TECC with temperature difference on the electrodes about 10°C.

Graph shows the linear I-V curve and symmetrical P-V curve of FT-IR in situ thermoelectrochemical cell. Shape of this curves is typical for TECCs based on $K_3[Fe(CN)_6] / K_4[Fe(CN)_6]$ electrolyte.

5. Concluding remarks
The results of the experiment showed that the thermoelectrochemical cell for in situ IR Fourier spectroscopy functions in accordance with the requirements, and the method used allows obtaining information on processes occurring on the electrodes and in the electrode region.

The results obtained during the study allow to plan and predict experiments on the study of changes in electrode materials in the redox process in thermoelectrochemical cell.

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