



Short communication

Rhenium exchange current density and transfer coefficient in the $\text{KF-KBF}_4\text{-B}_2\text{O}_3$ molten salt

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Abstract

The present paper is devoted to the study of the exchange current density of Re transfer in the high-temperature molten salt system using the Tafel dependencies. This data allowed precise information on the electrochemical behavior of the reaction mechanism. The exchange current density of the redox $\text{Re}^0/\text{Re}^{7+}$ pair was found to be $381.27 \mu\text{A cm}^{-2}$ at 773 K at 1 wt.% of KReO_4 in $\text{KF-KBF}_4\text{-B}_2\text{O}_3$ molten salt. The cathode transfer coefficient was calculated using the inclination angle tangent of Tafel graphs.

Keywords

Refractory metal; electroreduction; electrolysis; Tafel plots; kinetic parameters

Introduction

Rhenium (Re) has attracted the attention of researchers for its unique combination of properties, including a high melting point (3180 °C), high modulus of elasticity, high strength at elevated temperatures, good ductility and excellent corrosion resistance [1]. In addition, among refractory metals, Re is the only element that does not form carbides [2]. The coatings are applied to the surface of the carbon substrate either as a protective coating to increase the abrasion resistance or as a transition layer between the iridium coating and carbon to improve their compatibility. Interest in Re has recently significantly grown due to its widespread use in high-temperature applications, such as Re/Ir combustion chambers for liquid rocket engines [3,4].

Electrodeposition from molten salts is a conventional method for producing refractory metals. This method allows obtaining dense and smooth Re coatings on substrates of complex shapes. Moreover, it is a cost and highly efficient process [4]. In addition, the Re coating with a thickness of several micrometers can be obtained by electrodeposition in molten salts. Vinogradov-Zhabrov *et al.* [5] studied the electrodeposition of Re from NaCl-KCl-ReCl_4 melts in the temperature range from 680 to 970 °C at the cathode current densities ranging from 5 to 250 mA cm^{-2} . The effect of electrolysis parameters on the texture of the Re coatings growth was investigated. Esina *et al.* [6,7] analyzed the

epitaxial growth of the Re layer electrodeposited from CsCl-Cs₂ReCl₆ melts on monocrystalline, polycrystalline Re and tungsten substrates of various orientations. Chernyshev *et al.* [8-12] investigated the electrodeposition of rhenium coatings from fluoroborate melts KF-KBF₄-B₂O₃-KReO₄. In previous studies, researchers focused mainly on the effect of the electrolysis conditions and type of substrate on the texture of the growing Re layer or electrochemical process [13,14]. However, the kinetic parameters of the electrodeposition process have not been analyzed.

The exchange current density and transfer coefficient are important electrochemical parameters for modeling and evaluating the electrodeposition process using the Butler-Volmer equation. Since the exchange current density determines the degree of reduction when the redox potential is applied, it is important to measure the exact value of this variable. Currently, there is a lack of data on the exchange current density and the Re transfer coefficient in salt melts. In this study, the exact exchange current density and rhenium transfer coefficient were measured using two electrochemical methods in the molten KF-KBF₄-B₂O₃-KReO₄ salt. In addition, the dependence of the exchange current density on the concentration of KReO₄ was investigated by obtaining the exchange current densities at different concentrations.

Experimental

Equipment

All electrochemical experiments were carried out in the ambient atmosphere in a glassy-carbon crucible (SU-2000). The temperature of the electrolyte was maintained using a resistance furnace. The furnace temperature was controlled simultaneously during the experiments; the measurement error was ± 1 °C. For electrochemical studies, an Autolab PGSTAT-302N potentiostat (Metrohm, Switzerland) with the Nova 2.1.5 software package was used, and ohmic losses were hardware compensated.

Platinum wire with a diameter of 1 mm and an area of 0.36 cm² was used as a working electrode, and rhenium stacks are used as a counter electrode. A Re electrode immersed into the KF-KBF₄-B₂O₃-KReO₄ (6 wt.%) melt in the argon atmosphere (99.998 wt.%) served as a reference electrode. The electrolyte of the reference electrode and the melt under study were separated by a diaphragm made of pyrolytic boron nitride. The experimental setup is described in detail elsewhere [12].

Chemicals

The KF (37.28 wt.%) - KBF₄ (40.39 wt.%) - B₂O₃ (22.33 wt.%) melt was prepared in a glassy-carbon container by fusing weighted portions of individual salt powders. Commercial chemically pure individual KF, KBF₄ and B₂O₃ salts were provided by Vekton Company, Saints-Petersburg, Russia. Rhenium concentration (1 to 6 wt.%) in the melt was set by direct addition of potassium perrenate (KReO₄) powder. The prepared reagents were subjected to chemical analysis using optical emission spectrometry with inductively coupled plasma iCAP 6300 Duo (Thermo Scientific, USA).

Results and discussion

Cyclic voltammetry

Figure 1 shows cyclic voltammograms at potential scan rates from 0.1 to 1 V s⁻¹. In the cathodic region, two cathodic peaks can be observed. The nature of the obtained dependencies is similar to previously published work [12]. In the work [12], the authors conclude that both peaks correspond to the reduction reaction of rhenium ions, and according to the results of calculations and potentiostatic electrolysis, reduction in both the first and second peaks occurs with the transfer of 7 electrons. The authors write down equations (1) and (2) for the process:



During the reaction occurring at the first peak, 1 mole of rhenium metal and 2 moles of rhenium-containing mesaperenate ions are formed. With further polarization, the reduction reaction of mesaperenate to metallic rhenium begins:

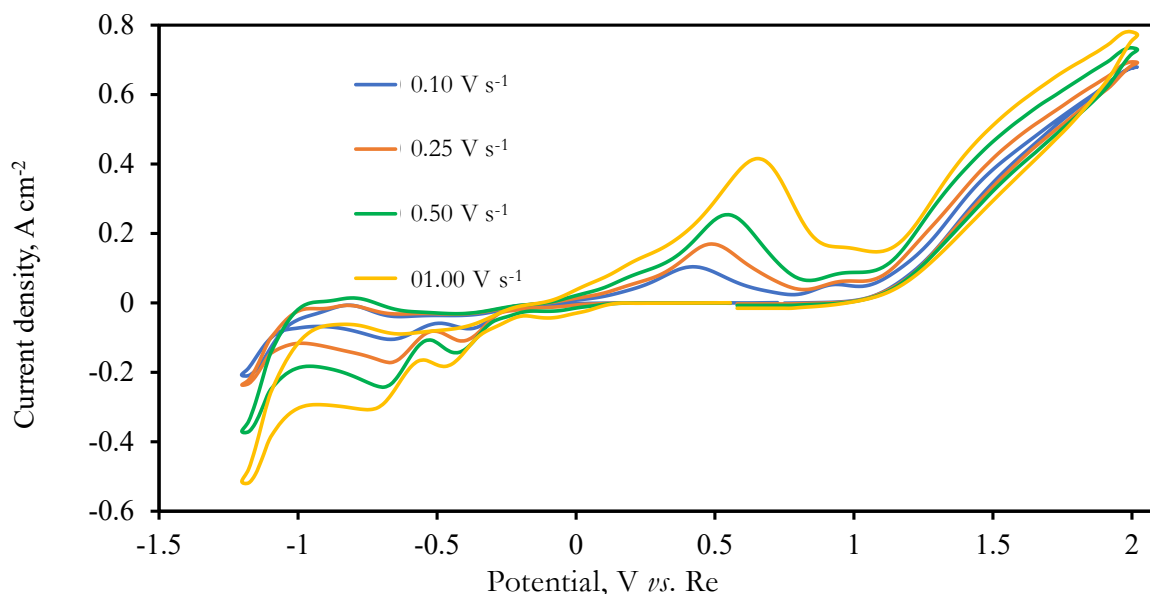


Figure 1. Cyclic voltammograms of the $\text{KF-KBF}_4\text{-B}_2\text{O}_3\text{-1 wt.}\% \text{KReO}_4$ melt recorded at different potential sweep rates ranging from 0.1 to 1 V s^{-1}

The dependences of the peak current potentials on the rate of potential change (Figure 2a) have a slight deviation in the range of scan rates up to 1 V s^{-1} . This dependence is typical for both the first peak and the second. A slight deviation of the peak current potential indicates that the processes occurring at both peaks are quasi-reversible.

In addition, the peak current was confirmed to be linearly proportional to the square root of the scan speed according to the Berzins-Delahay equation (equation 3), as shown in Figure 2B [15,16]

$$i_p = 0.611nFC \left(\frac{nF}{RT} \right)^{1/2} D^{1/2} \nu^{1/2} \quad (3)$$

where i_p is the peak current density (mA cm^{-2}), ν is the scan rate (mV s^{-1}), C is the bulk concentration of the reducible ion (mol cm^{-3}) and D is the diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$).

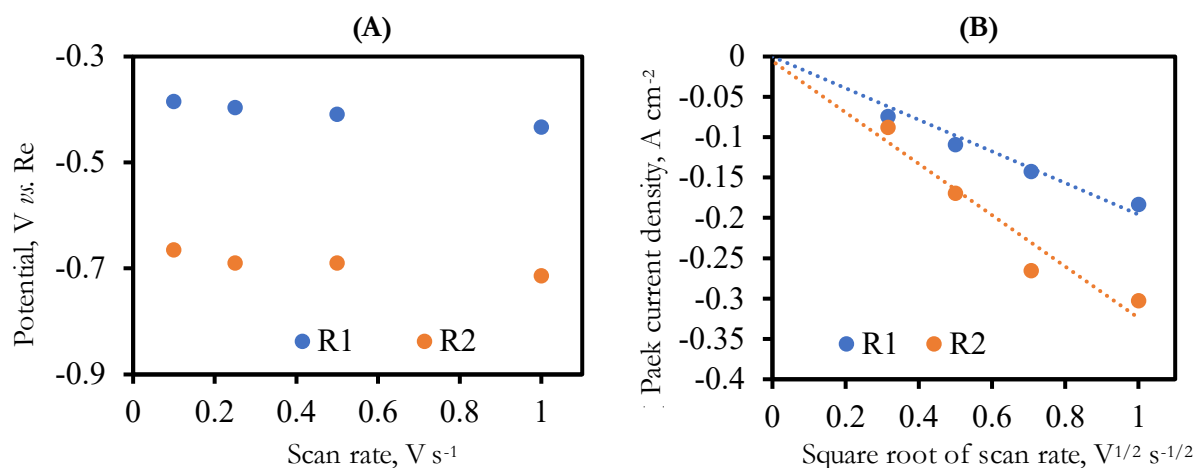


Figure 2. (A) Peak potentials and (B) peak current densities of the $\text{KF-KBF}_4\text{-B}_2\text{O}_3\text{-1 wt.}\% \text{KReO}_4$ melt recorded at potential sweep rates up to 1 V s^{-1}

Exchange current density and transfer coefficient

The exchange current density of the $\text{Re}^0/\text{Re}^{7+}$ redox pair was obtained using the Butler-Volmer equation. The Butler-Volmer equation (Eq. 4) describes the current at the electrode in terms of the overvoltage (η) and the simultaneously occurring anodic and cathodic currents [17]:

$$i = i_0 \left\{ \exp \left[\frac{(1-\alpha)nF}{RT} \eta \right] - \exp \left[-\frac{\alpha nF}{RT} \eta \right] \right\} \quad (4)$$

where $i / \text{A cm}^{-2}$ is the measured current density, $i_0 / \text{A cm}^{-2}$ is the exchange current density, α is the charge transfer coefficient, n is the number of electrons transferred in the oxidation/reduction reaction under consideration (in this case, $n = 7$), F is the Faraday constant (96485 C mol^{-1}), R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T / K is temperature, η / V is the overvoltage.

In the case of the large cathode overvoltage, when the anode current can be neglected, the Tafel approximation of the Butler-Volmer equation (Eq. 5) is valid [18].

$$i = -i_0 \exp \left[-\frac{\alpha nF}{RT} \eta \right] \quad (5)$$

To determine the exchange current density, the polarization curves were reconstructed in semilogarithmic coordinates:

$$\ln i = -\frac{\alpha nF}{RT} \eta + \ln i_0 \quad (6)$$

Using the Tafel plot, the cathodic transfer coefficient α of reactions (1) and (2) was calculated. To identify the effect of scan rate on the exchange current density and transmission coefficient, a Tafel diagram (Figure 3) was constructed with different scan rates from 0.1 V s^{-1} to 1 V s^{-1} .

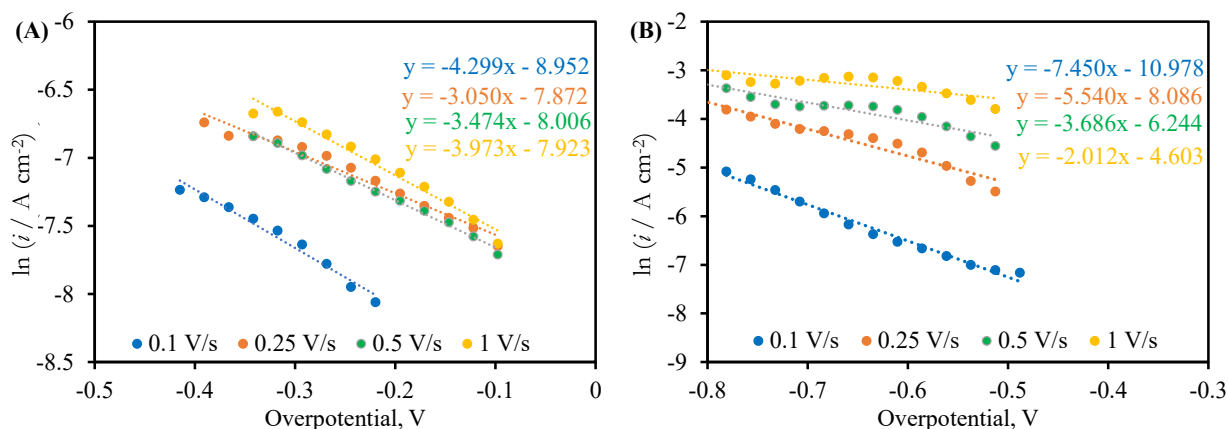


Figure 3. Tafel graphs for 1 wt.% KReO_4 in the $\text{KF-KBF}_4\text{-B}_2\text{O}_3$ molten salt at 773 K and different potential sweep rates up to 1 V s^{-1} . Reaction proceeding according to: (A) Eq. (1) and (B) Eq. (2)

Experiments presented in Figure 4 show that the exchange current density depends linearly on the scanning speed. The transfer coefficients of the $\text{Re}^0/\text{Re}^{7+}$ reaction also depend on the scan speed from 0.1 to 1 V s^{-1} . Subsequently, the concentration dependence of the exchange current density was studied.

Figures 5a and 5b show Tafel plots for the reduction reaction of rhenium according to equations (1) and (2), respectively, in molten salt $\text{KF-KBF}_4\text{-B}_2\text{O}_3$ with adding 1-6 wt.% KReO_4 at 773 K. According to Eq. (5), the current at the intersection point on the natural logarithmic scale is the value of the exchange current.

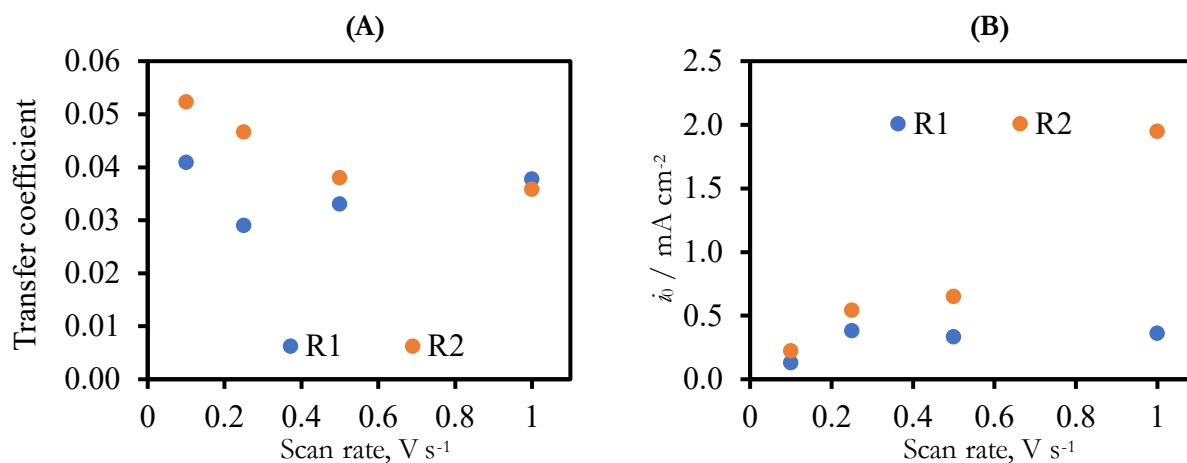


Figure 4. (A) Transfer coefficients and (B) exchange current density of the Re^0/Re^{7+} for 1 wt.% $KReO_4$ in the $KF-KBF_4-B_2O_3$ molten salt at 773 K and different potential sweep rates up to $1 V s^{-1}$

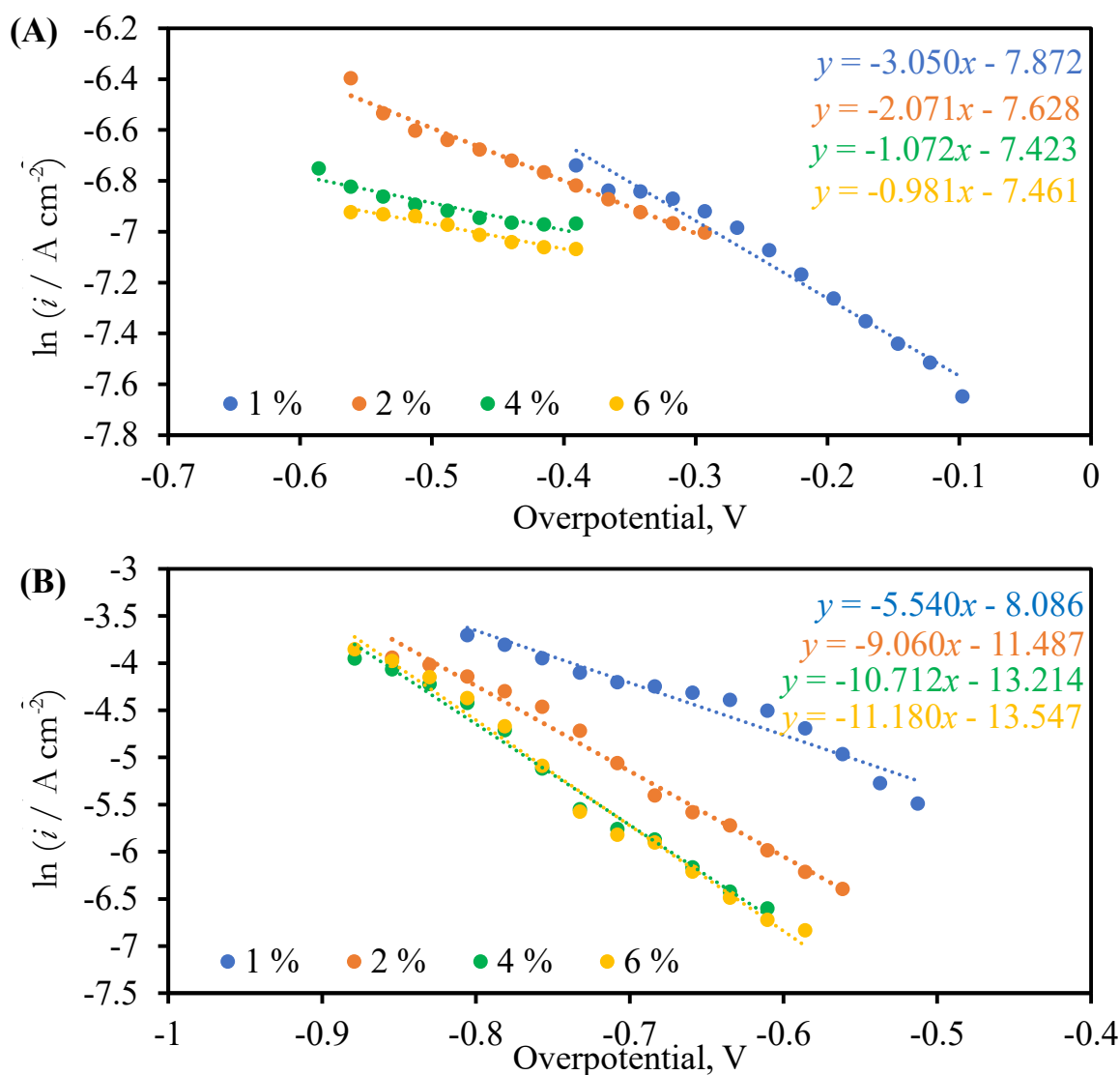


Figure 5. Tafel graphs for different concentrations (1-6 wt.%) of $KReO_4$ in the $KF-KBF_4-B_2O_3$ molten salt at 773 K. Reaction proceeding according to: (A) Eq. (1), and (B) Eq. (2)

The exchange current density is also affected by the concentration of potassium perrhenate. To investigate how concentration affects the exchange current density, Tafel plots of $KReO_4$ were obtained at different concentrations in $KF-KBF_4-B_2O_3$ molten salt. The concentration range of $KReO_4$

was controlled from 1 to 6 wt.%. With the exception of sample concentration, all experimental conditions remained constant. The measurements were carried out at 773 K. Figure 6 shows the exchange current densities when the KReO_4 concentration changes.

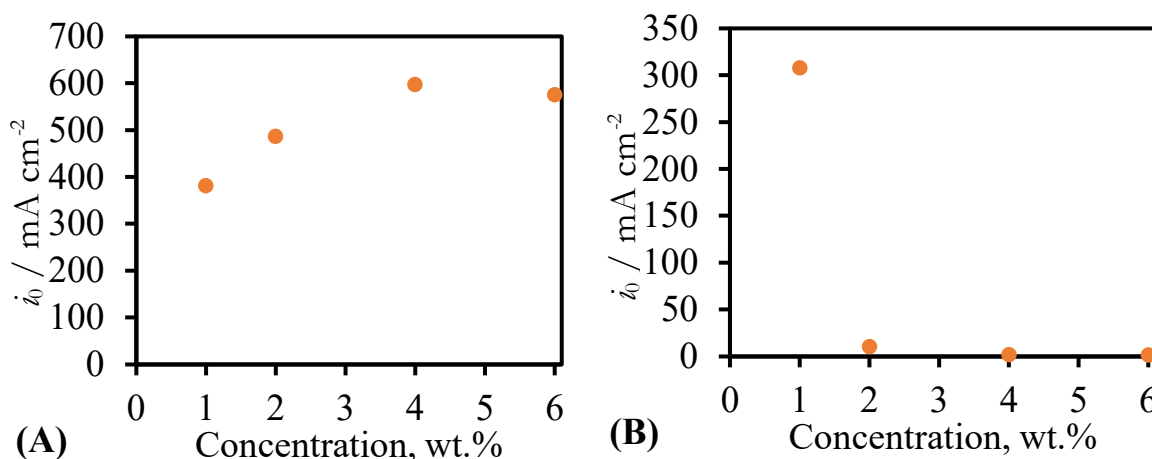


Figure 6. Dependence of exchange current density on KReO_4 concentration in the $\text{KF-KBF}_4\text{-B}_2\text{O}_3$ melt. Reaction proceeding according to (A) Eq. (1) and (B) Eq. (2).

As shown in Figure 6, the exchange current density, as expected, depends on the concentration for reaction (1), while for reaction (2), the exchange current density decreases sharply with increasing concentration and becomes almost constant with a further increase in concentration.

Conclusions

In this study, the exchange current density and transfer coefficient of Re in a high-temperature molten salt system were investigated using Tafel plots to gain a more accurate understanding of the electrochemical behavior and reduction reaction.

The concentration dependence of the current density was obtained for the redox couple $\text{Re}^0/\text{Re}^{7+}$ at 773 K in the $\text{KF-KBF}_4\text{-B}_2\text{O}_3$ electrolyte. It has been established that the exchange current density does not vary linearly for both reaction (1) and reaction (2).

Summarizing the data obtained, we can make the assumption that the process of rhenium reduction in a molten salt composition has a more complex mechanism than that presented in equations (1) and (2).

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