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Electrochemical impedance characterization on catalytic carbon gasification reaction process

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HIGHLIGHTS

- New application field of electrochemical impedance spectroscopy.
- Fast and in-situ experimental characterization of catalytic gasification process.
- Complex permittivity simulation considering elementary reactions.

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ABSTRACT

The dielectric characteristics of the solid fuels have close relation with gasification process. Electrochemical impedance spectroscopy (EIS), is applied for measuring the dielectric characteristics of solid carbon fuels in catalytic and non-catalytic gasification systems. Compared with kinetic experiments at different gasification temperatures (775, 800 and 825 °C) for both catalytic and non-catalytic gasification, EIS spectra is proved to be an effective method to characterize the carbon gasification reaction characteristics in situ with high sensitivity, especially at low carbon conversion ratio. An elementary reaction model for potassium catalyzed carbon gasification combined with a dielectric mixture equation for the simulation of complex permittivity is developed. The modeling results agree well with the experimental data. The dielectric property of catalyzed solid carbon fuels provided by EIS reveals that the polarization intensity contains effective information of gas adsorption and heterogeneous chemical reaction. EIS can possibly be applied as a new methodology in investigating the catalytic carbon gasification reaction and transport processes.

1. Introduction

Catalytic carbon gasification has been extensively studied for its important role in lowering the operating temperature of gasification process [1]. Fixed bed experiments or TGA (Thermal Gravity Analysis) experiments are usually used in investigating carbon gasification kinetics ascribing to their relatively simple setup and the wide applicability in different operating conditions [2–9]. However, one of the drawbacks of the fixed bed testing is the channeling volume effects which leads to errors in gasification kinetics studies due to mass transfer process [6]. In addition, the experimental detection of the gas product composition from gas chromatograph or mass spectrograph is actually not real-time signals but usually time-average signal because of the gas residing within the reactor and channels. TGA is effective for measuring carbon gasification kinetic data, however, it is constrained for gasification processes under high pressure and harsh experimental conditions, especially when operated in toxic gas atmosphere which commonly happens during carbonaceous fuels gasification process.

Electrochemical impedance spectroscopy (EIS), also known as dielectric spectroscopy, is an experimental technology for characterizing the dielectric properties of a system in frequency domain or time domain [10]. It reveals abundant characteristics about transient processes like dielectric behavior, mass transfer, electrochemical reactions, etc. [11]. Therefore, EIS nowadays is widely applied in various fields of electrochemical engineering, biosciences, corrosion, etc. [12]. Conway [13] succeeded in applying EIS to investigate the interactions between functionalities

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at activated carbon surface and metal ions when studying the electrochemical supercapacitors. Combining calorimetric and dielectric measurements, Keller et al. [14] used EIS to determine the absolute masses of gas adsorbed on porous solid materials. Keller et al. [12] also experimentally demonstrated the dielectric characteristics was correlated with gas adsorption phenomena of activated carbon. Rubel et al. [15] further applied EIS technique as a monitor to detect the steam adsorption characteristics on activated carbon sorbent.

Based on above applications of EIS technique, it can be expected that the EIS can be used in characterizing the catalytic carbon gasification from the perspective of electrochemistry to develop the relations between complex dielectric features and gasification kinetics of catalyzed carbonaceous fuels. In this study, the capability of applying EIS technique in investigating the carbon gasification process is examined by in-situ measuring EIS and kinetics characterizations of catalytic carbon gasification experiments at different temperatures. Both dielectric impedance and gasification kinetics models are developed through the combination of a proposed elementary reaction model of catalytic carbon gasification and a complex dielectric mixture theory.

2. Experiments

2.1. Experimental setup

As shown in Fig. 1(a), a sealed single chamber reactor (35 cm in height and 5 cm in diameter) was placed in a tube furnace. The gasifying agent CO_2 and protecting gas argon (Ar) controlled by mass flow controllers (MFC Sevenstar Electronics Co., LTD, Beijing) were mixed before introduced into the reacting chamber, while the production gases were introduced into a mass spectrograph(QGA, Hiden, UK) for measuring gas composition. An electrochemical workstation (IM6ex, Zahner–Elektric GmbH, Kronach, Germany) was used to detect the complex alternating current (AC) impedance of the carbon bed which is a tiny capacitor-like electrochemical system depicted in Fig. 1(b). The carbon bed was packed in an insulated ceramic ring with diameter of 10 mm and height of 4 mm. Two porous steel planes were fixed onto two sides of the ceramic ring by ceramic bolts, serving as the electrodes for detecting the dielectric polarization. Moreover, gold wires and platinum nets connected with the steel planes were used to collect the current signals for in-situ EIS characterization.

2.2. Catalytic carbon gasification experiments and EIS tests

A kind of commercial activated carbon (Wenxian Hengsheng Co., Ltd., China) was used as the typical carbonaceous fuel, diameter of which was 50 μm to 100 μm after lapping and sieving. Pure potassium carbonate (K_2CO_3) was used as precursor of the catalyst which was added by impregnation method, at a ratio of metal atom to carbon of 1:10 by weight [20]. The carbon fuel sample was then added into a sample of K_2CO_3 dissolved in de-ionized water. After stirred for 5 h and kept for 24 h, the mixed sample was then dried at 70 °C in an oven for another 24 h.

Before experiments, 0.3 g carbon sample with catalysts was packed in the ceramic ring hung by two golden wires in the sealed chamber. After heated up at a fixed rate of 10 °C min^{-1} and under a continuous argon flow rate at 20 sccm (standard-state cubic centimeter per minute), the carbon bed was exposed in a CO_2 atmosphere with CO_2 flow rate at 100 sccm at temperatures of 775, 800 and 825 °C. During the programmed heating up process, EIS test was conducted in the frequency range from 100 Hz to 10^6 Hz to determine the carbon fuel AC impedance change with increasing temperature. Then, the carbon fuel impedance was detected at

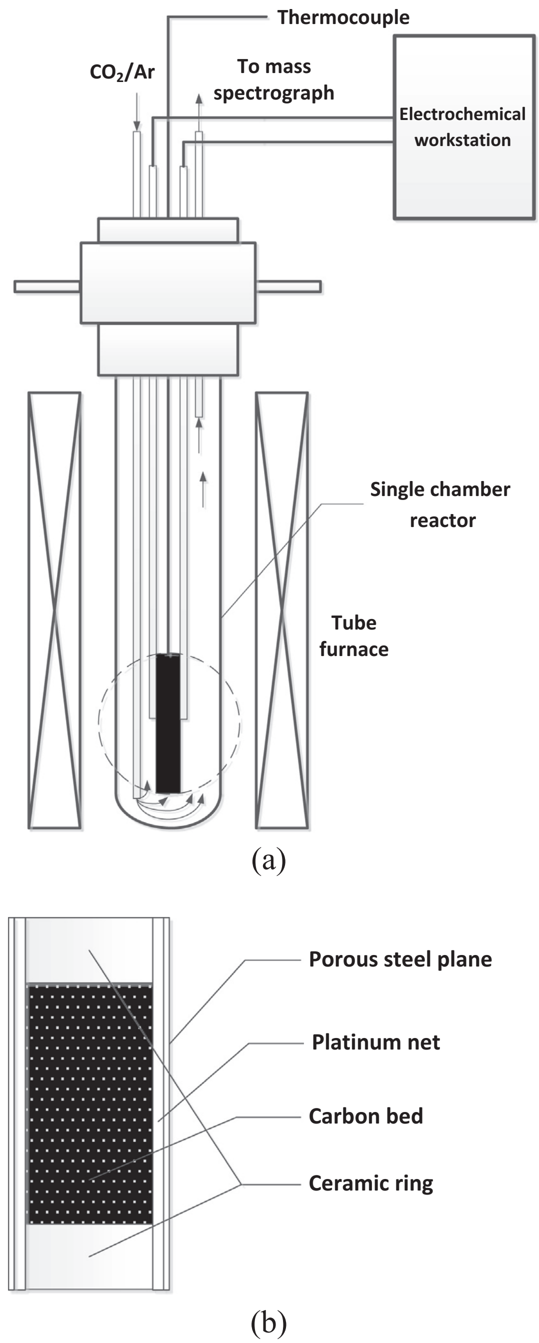

Fig. 1. Experimental apparatus: (a) overall system setup used for carbon gasification experiments, EIS and kinetics online measurements, consisting of a single chamber reactor and other auxiliary detecting parts; (b) close-up of the capacitor-like carbon bed used for in situ EIS test.

constant frequency for detecting the gasification characteristics at a fixed temperature. EIS measurements were completed by collecting the current response to a perturbation signal of sinusoidal voltage $E = E_0\sin(\omega t)$. The corresponding complex AC impedance $Z(\omega)$ was readily accessed by ratio of input voltage over measured current. By altering the voltage frequency in the interesting bandwidth, the impedance was expressed by its real and imaginary parts together, i.e. $Z(\omega) = Z' - jZ''$. Typically, the AC impedance can be demonstrated by Nyquist plot or Bode plot to detect the underlying dielectric characteristics of the system.

In addition, non-catalytic gasification experiment was conducted at 825 °C as the control case. The composition of the