Molecular dynamics simulations of the coke formation progress on the nickel-based anode of solid oxide fuel cells

Haibin Lu, Dong Hua, Taosif Iqabl, Xiongwen Zhang⁎, Guojun Li, Di Zhang

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ABSTRACT

Coke formation on anode of solid oxide fuel cells (SOFC) can lead to SOFC performance degradation or even failure. This paper investigates transfer mechanism of carbon atoms in coke formation process on nickel-based anode using the reactive force field molecular dynamics simulation (ReaxFF-MD). The simulation results show that the transfer processes of carbon atoms in methane reforming are composed of three stages, and the alkyl makes formation of coke easier on the surface of Ni(100). The driving force of the carbon atoms diffusion into Ni (100) changes from the carbon concentration difference to the chemical potential difference, which leads to the generation of a new phase of carbon and the structural damage of the SOFC anode. The structural changes of Ni (100) during the carbon atom transport and precipitation are simulated and analyzed to reveal the chemical reaction mechanisms of coke formation, and provide theoretical foundation for optimal design in materials and operating parameters of SOFC anode.

1. Introduction

Solid oxide fuel cell is a high-temperature fuel cell (600 °C–1000 °C) with high efficiency and low emission advantages. A high operating temperature poses risk of coke formation in the catalytic reforming of hydrocarbon fuels (e.g. methane, propane and butane, etc.). Coke formation on anode can make nickel electrochemically oxidized [1]. It can also destroy the topological structure of the triple-phase-boundary (TPB) in the anode, which leads to performance degradation of SOFC and makes SOFC stack efficiency very low [2]. The key factor is to understand the issue of carbon deposition by investigating the mechanism of carbon precipitation and transport.

Current research on inhibiting coke formation mainly attaches great importance to the controls of the operating conditions and gas compositions of fuel. For example, by introducing a quantity of oxygen into hydrocarbon fuel was proved to be helpful in removing the coke [3]. Many researches also illustrated operating at higher steam to carbon ratios (S/C) can inhibit the formation of coke [4,5]. A Control-oriented Dynamic Model Adapted to Variant Steam-to-carbon Ratios for an SOFC with Exhaust Fuel Recirculation. The core concept with the aforementioned methods is to enhance the responsive reaction by diluting carbon concentration in the fuels. Choudhary and his collaborators [6,7] constructed a three-dimensional transient model, using CFD and FEM methods to study the air ratio and temperature field impact to carbon deposition.

In the recent years, researchers began to use molecular dynamics (MD) simulation method to study the process of hydrocarbons cracking into carbon clusters with nickel catalyst. Nielson and his partners used ReaxFF-MD to study the process of amorphous carbon converting to carbon nanotubes and other substance with nickel catalysis under certain conditions [8]. Using the retrained force field parameters, Somers et al. [9–11] studied the mechanism of carbon formation from hydrocarbon plasma catalyzed by different types of nickel. Their study results reveal CH3 has high adsorption rate on all kinds of nickel surface. Different types of nickel in the process of reaction have different reactivity like the adsorption rate of free radical on Ni(100) is higher than that of Ni(111) [9–11]. Lu et al. studied the catalytic dehydrogenation reaction mechanism of aromatic compounds on Ni(111) surface in the chemical vapor deposition reactor [12]. Merinov et al. developed force field parameters to simulate ions transport and chemical reactions on the triple-phase interface (TPB) [13]. This study established the basis of nickel-based catalytic reactions, including the reaction of carbon with relevant elements, coke formation and the formation process of carbon clusters.

Accordingly, to study SOFC coke formation, the transition process of carbon atom from carbon compounds to carbon clusters should be investigated. It contains the processes of the catalytic cracking of hydrocarbon, carbon atoms diffusion in nickel and carbon atom gathering into clusters. Considering that the internal reforming of hydrocarbon fuel in SOFC is usually at high temperature and the reforming reaction
rate is too fast to measure, it is difficult to obtain the detail thermal reforming reaction by experiments. For example, Fan et al. [16] studied the carbon deposition process of methane on Ni-YSZ surface by means of experimental thermodynamics simulation and numerical simulation. However, the physical damage of anode cannot be discussed deeply because of the limitation of the research method [14]. Molecular dynamics simulation is an effective method to study the mechanism of coke formation process. Compared to the traditional molecular dynamic simulations, ReaxFF-MD takes molecular bond order into account in the simulations. Therefore, it can reveal the course of the chemical bond breaking and formation in the chemical reaction. Meanwhile, as the computational cost of ReaxFF-MD is inexpensive, it can be used to calculate larger time scale than that of quantum chemistry and primary molecular dynamics calculation while get the same precision as quantum chemistry [15]. Therefore, ReaxFF-MD was widely used in the complex chemical reactions, such as the rapid reaction of explosions, the thermal cracking and combustion, the catalytic reactions under extreme conditions, and the structural transformation of state aggregation [16]. Merinov et al. [17] modeled chemical reactions, diffusion, and other physicochemical processes at the fuel/Ni/YSZ interface by simulating amorphization of the Ni surface, partial decohesion (delamination) at the interface, and coke forming. The products obtained by ReaxFF MD properly describes complex physicochemical processes, such as the oxide-ion diffusion, fuel conversion, water formation reaction, coking, and delamination, occurring at the TPB.

Duin et al. [18,19] applied the ReaxFF to describe the proton diffusion in crystalline and across grain boundaries of BYZ. Their research results validated the use of ReaxFF to study transport properties of the membranes. They also validated it for fuel cell applications to predict the oxygen ion diffusion coefficient in ytria-stabilized zirconia as a function of temperature. It was proved the usefulness of ReaxFF to model the transport of oxygen ions through the YSZ electrolyte for SOFC.

In this paper, we utilize the ReaxFF-MD to develop the model of chemical reaction to investigate the precipitation and diffusion process of carbon atoms on Ni(100). By examining the carbon atoms migration process, tracing the structural evolutions, we were able to investigate the mechanism of the occurrence and growth of coke on the anode. The simulation results are in agreement with the experimental results and provide theoretical support for the improvement in operating parameters of SOFC anode.

2. Simulation methodology

2.1. Models construction

Three Ni(100) models so-called Model-1, 2, and 3 with 125 nickel atoms are defined for the simulations. A vacuum layer filled by hydrocarbon molecules was built on the surface of Ni(100). Different types and numbers of hydrocarbon molecules in the vacuum layer are simulated to investigate the influence of hydrocarbon molecule structures on the coke formation. Therein, Model-1 contains 54 methane molecules surrounding Ni(100) models (see Fig. 1a), Model-2 includes 30 methane molecules and 24 methanol molecules (see Fig. 1b) and model-3 contains 30 methane molecules and 12 ethanol molecules (see Fig. 1c). In the case study of Model-1, the hydrogen generated from the chemical reactions are removed after 250 ps of simulation, thus avoiding the hydrogen interference to the carbon cluster forming process and therefore being able to reveal the mechanism of the carbon cluster formation [20]. Additionally, another model (Model-4) containing 400 nickel atoms of Ni(100) with 200 methane molecules is defined to show the details of the carbon atoms diffusion progress in Ni (100).

2.2. Simulation details of ReaxFF MD

ReaxFF-MD considers the system energy composed of various partial energy contributions, such as bond angle, dihedral angle, conjugate, Coulomb, van der Waals and adjustments. They are similar to empirical nonreactive force fields (Eq. (1)). ReaxFF-MD takes bond order as the core, and transforms the chemical bonds (BO$\sigma$, BO$\pi$, BO$\Delta\pi$) as function of $r_{ij}$ (Eq. (2)) [15]. According to the bond orders of any two atoms in the simulation progress, ReaxFF-MD determines the connectivity between atoms and simulates the bond formation and cleavage of chemical reactions. The molecule structures are modified on the basis of the atomic valence change, interatomic bonding method, conjugate and non-conjugate structure change, intramolecular forces and nonbonding effort. The model of ReaxFF-MD is a close simulation to the real situation.

$$E_{\text{System}} = E_{\text{bond}} + E_{\text{tip}} + E_{\text{under}} + E_{\text{val}} + E_{\text{non}} + E_{\text{ooh}} + E_{\text{C2}} + E_{\text{triple}} + E_{\text{quad}} + E_{\text{coulomb}}$$

$$BO^\sigma = BO^\pi + BO^{\Delta\pi} = \exp \left[ \rho_{bo\sigma} \left( \frac{r_{ij}}{r_0} \right)^{\rho_{bo\sigma}} \right] + \exp \left[ \rho_{bo\pi} \left( \frac{r_{ij}}{r_0} \right)^{\rho_{bo\pi}} \right] + \exp \left[ \rho_{bo^{\Delta\pi}} \left( \frac{r_{ij}}{r_0} \right)^{\rho_{bo^{\Delta\pi}}} \right]$$

A ReaxFF program package referred to [15,21] is used to conduct the ReaxFF-MD simulations in this work. The sets of the ReaxFF force field parameters for hydrocarbon were taken from the study of Merinov et al. [13]. This study focuses on the methane catalytic decomposition mechanism in the high temperature. According to the reaction thermodynamics can promote methane reforming in the positive direction if the temperature is increased but Sørensen’s work of temperature accelerating kinetics based on harmonic transitional state theory demonstrate higher temperature can accelerate coke formation without a accuracy. Qualitatively, the mechanism of coke formation does not change with the increase of simulation temperature. Thus, we set the
simulation temperature at 2000 K to balance both accuracy and time scale. The ReaxFF-MD simulations were performed with NVT ensembles, periodic boundary condition and Berendsen temperature control method [22]. The damping parameter and time step were set to be 0.1 ps and 0.25 fs, respectively.

3. Results and discussion

3.1. The progress of coke formation

To understand the micro-diffusion mechanism of coke formation, it is necessary to find the key factors that influence on the migration process of carbon atoms during the coke formation process. The simulations on the carbon migration in this process can clearly illustrate the diffusion mechanism at molecular level. This makes up for the inadequacy of experimental observation. Experimental results from reference [23] showed that the anode performance was considerably decreased due to carbon absorbed on nickel surface during short period of time. The main purpose of this study is to look into the process on molecular level to understand the root cause of coke formation. Fig. 2 is an overview of the migration process of carbon atoms in the methane molecules on Ni (100) surface, which clearly shows the migration route of carbon atoms. By forming H–Ni bond between one hydrogen atom of methane molecule and nickel Ni(100), most of methane molecules completely cover the surface. After this (see at 23.5 ps in Fig. 2-vi), carbon atoms begin large-scale migration to the internal area of Ni (100). The migration process can be divided into two steps: methane adsorption on the surface of Ni(100) (Fig. 2i–v) and carbon atom diffusion (Fig. 2vi–vii).

Fig. 3 shows the methane and hydrogen product distributions and the change rate of methane during methane reforming reactions from the simulation of Model-4. We calculated the change rate of methane during methane reforming reactions by using a 19th order equation fitted for the methane distribution curve. As we can see from Fig. 3, 20 methane molecules are adsorbed by Ni(100) while only 18 methane molecules are adsorbed in the subsequent 70 ps in first 23.5 ps. Corresponding with Fig. 3, the increase of carbon content in Ni(100) at the start of 23.5 ps is mainly caused by the adsorption of methane on Ni (100) surface. The adsorption of methane on nickel is the beginning stage of coke formation. With the increase of adsorbed methane on Ni (100) surface, the increased space steric hindrance hampers the proceeding of methane adsorption. As shown in Fig. 3, the carbon atoms immediately diffuse to the internal of nickel body as soon as the methane is adsorbed on the surface of Ni(100). However, the diffusion rate of carbon atoms in the substrate is far less than the adsorption rate of methane in the initial stage, and leads to a dramatic decrease of increasing carbon atoms in the subsequent reaction in Ni(100). Since then, carbon atoms diffuse to the internal area of Ni(100) gradually and the removal of hydrogen from the Ni(100) surface results in reduction of space steric hindrance on Ni(100) surface, and adsorption progress of methane restarts, and this is the main reason the adsorption rate of methane frequent changes since 23.5 ps (see Fig. 3). Apparently, the mass transfer process of carbon atoms in the methane reforming reaction on the nickel-based catalyst can be divided into the processes of adsorption, diffusion, and repeated adsorption. Somers et al. [10] studied the adsorption activity of carbon on the surface where the bonded carbon is reduced and the adsorption sites for new coming carbon molecule must be changed. This slow down the carbon atom's adsorption and diffusion progress. Controlling the adsorption rate at the first place will lead to improve the catalytic reforming reaction and decrease in coke formation.

3.2. Processes of adsorption

The atomic migration processes of catalytic reforming for hydrocarbon fuels on Ni(100) surface is captured from the ReaxFF-MD simulations. Fig. 4 shows the methane evolution process in the reforming reaction. As we can see from Fig. 4, the chemical adsorption of methane on the Ni(100) surface is a serial processes composed of the C–H bond
rupture, hydrogen generation from the alkyl radical free radicals, and Ni–C bond formation. When a hydrogen atom is close enough to a nickel atom, a Ni–H bond will be formed (Fig. 4-i), which narrows the distance between the carbon atoms and nickel atoms, and causing the formation of Ni–C bond (Fig. 4-ii). The C–H bond has extremely unstable molecular structure at high temperatures and can be broken easily, which causes methyl to be bonded on the Ni(100) surface. The Ni–C bond makes the carbon atoms closer to the surface of nickel, which results in the formation of C-H-Ni bond (Fig. 4-vi). The removal of hydrogen atoms leaves behind Ni–C bonds.

In order to clarify the impact of molecular structure change on the coke formation, we use methanol and ethanol to replace methane (Model-2 and Model-3) in the simulations. These two cases illustrate the coke formation mechanism for different molecular structure and functional groups of hydrocarbons. Although the molecular structure of methanol is close to methane, the catalytic mechanism for methanol reforming reaction is quite different from that of methane. As shown in Fig. 5, the hydrogen atoms in the transitional C–H–Ni bond at the beginning of the reaction come from the alcoholic hydroxyl group rather than the methyl. The generated methyl is close to the surface of Ni(100) and transferred to Ni–C–H bonds. Subsequently, make the carbon atom bonds bonded on the surface of Ni(100). High temperature accelerates the transition process from the Ni–C–H bond to rupture alcoholic hydroxyl and Ni–H bond, and generated H₂, H₂O and other free radicals. Some H₂ and H₂O generated water which has been recognized to affect the subsequent coking process [24,25]. The reaction of alcoholic hydroxyl and Ni(100) limits the movement of ethanol molecules, which enables the hydrogen atom at a position of ethanol to be easily combined with Ni atom, leading to a series catalytic dehydrogenation of ethanol, and make α carbon atom bonded with Ni(100) surface.

For ethanol reforming reaction, a carbon chain is composed of two carbon atoms bonded on Ni(100) surface, which is the basic difference between methanol and methane systems. The influencing factors of the adsorption reaction on the internal migration process of carbon atoms in Ni(100) are also different as the energy is larger for C–C bond than of C–Ni. The C–C bond is not easily broken during the diffusion process of the carbon atoms in Ni(100). Thus, The resistance for the bonded carbon atoms diffusion in Ni(100) is significantly high, and more and more carbon atoms accumulate on the surface of Ni(100). Therefore carbon clusters are formed on the surface of Ni(100) when the reforming reaction is proceeding.

The key reactions that influence the mass transfer process of carbon atoms in nickel can be revealed by observing the rate of carbon content in the Ni(100). As shown in Fig. 6, the amount of carbon atoms adsorbed from ethanol system (Model-1) at the beginning of chemisorption is higher than those of methane and methanol systems. Because one absorbed ethanol on Ni(100) brings one more carbon atom than methanol. From the Fig. 7, we can see the amount of oxygen atoms adsorbed in the both systems is comparative in the first 5 ps of the reaction, and the decrease rates of the amount of methanol and ethanol are almost same (see Fig. 8). It suggests that the steric hindrance of Ni(100) surface is small at the early stage of adsorption reaction, because the methane does not influence the adsorption of ethanol and methanol and the reactivity of methanol and ethanol are approximately same. However, due to smaller molecular weight and lower adsorption steric, methane system has larger adsorption amount than that of methanol and ethanol systems at the early stage of the reaction. This can be seen at the beginning of 15 ps from Fig. 7, the adsorption amount of methanol in Model-2 and ethanol in Model-3 is larger than methane. The amount of adsorbed carbon atoms in the methane system is between the methanol and ethanol systems during the early reaction stage (see Fig. 6). However, a large number of adsorbed carbon atoms do not migrate into the crystal of nickel immediately, leading to steric hindrance and further increasing the influence on the adsorption reaction. Some absorbed methanol molecules in Model-3 begin to dissociate from.
Ni(100) surface, and some methane molecules are generated in this process. This explains why the number of methane rises at the early stage of simulation. As the carbon atoms are gradually migrated to the internal of Ni(100), the adsorption process of methane is restarted. Adsorption, desorption and migration process impact reaction mechanism the carbon precursor on Ni (100) surface. Wang and his collaborators found that there are three types of carbon, and the carbon source is methane catalytic cracking. Chen et al. [26,27] found that carbon can be divided into amorphous carbon (easy to remove) and graphite carbon (difficult to eliminate). Consider graphitization need longer reaction time, so carbon deposition precursor on Ni(100) surface is particularly important in the process of adsorption [28,29]. As it can be seen from Fig. 6, the amount of absorbed ethanol is far less than that of methanol in the later period of chemisorption adsorption. This is because the formation of steric hindrance is particularly prominent in the ethanol system. These untransformed molecules seriously impede the combination process of ethanol or other functional groups with Ni (100), which makes methane inefficient in the reforming reaction (see Fig. 8) and causes heavy coke formation on Ni(100) surface, and results in decreased ethanol reforming efficiency and catalytic failure of Ni (100) [30]. Therefore, there is a need to create an anode surface composed of numerous nanostructured interfaces that uses a chemical or electrochemical process to remove carbon on the exposed Ni surface. This will not impede the charge transfer process across the interfaces and allow achieving high-power output by using higher-order hydrocarbons.
3.3. Processes of diffusion

As shown in Fig. 9, after the methane molecules are adsorbed on the surface of Ni(100) with the cleavage and formation of Ni–C bond, the carbon atoms would gradually migrate to the internal of Ni(100). At the first step, a transition state with four Ni–C bonds and one Ni–H bond (see Fig. 9-ii) forms which is thermodynamically an unstable structure. Ni–H bond ruptures easily and results in the removal of hydrogen atom (see Fig. 9-iii). When the carbon atoms migrate to fill the gap between nickel atoms, this causes stretching effect of Ni–C bond (see Fig. 9-iv). However, since the distance between atoms gets closer, the “restless” carbon atoms can be easily combined with other nickel atoms to form new Ni–C bond. The crystal structure is then transformed into a transition structure with five Ni–C bonds (see Fig. 9-vi).

Ni(100) can be seen as a crystal lattice composed of nickel atoms as solvent, and the lattice gaps of crystal provide the space for the diffusion of carbon atoms. Consider the size of nickel atom is larger than that of carbon atom and the nickel crystal lattice is fixed, the diffusion of carbon atoms into the lattice gaps can be seen as a solid solution in nickel. At the initial stage of carbon diffusion, there are considerable amount of gap between the nickel atoms and a small number of carbon atoms in the system, each carbon atom is surrounded by the gap. A carbon atom will migrate from one gap to its adjacent gaps, which is called the gap diffusion. As shown in Fig. 6, the rate of the carbon atoms migration in nickel in the early stage of diffusion is greater than that of later stage. At the initial stage of migration process, the activation energy required for carbon atom diffusion is low. The probability of carbon being activated is very high because the crystal lattice of nickel has a high degree of symmetry and reaction temperature is high. Therefore, the carbon atoms easily leave its original position. This accelerates the diffusion of carbon atoms and increases the carbon concentration in nickel.

The face-centered cubic structure of Ni(100) has a large atomic gap, enabling the space of the gaps to be fully filled by the carbon atoms. Theoretically the largest amount of dissolved carbon could be more than 50% (by number of atoms). However, the amount of dissolved carbon in nickel is much less than this value. As shown in Fig. 9, when a carbon atom jumps from gap 1 to gap 2, those adjacent nickel atoms have to be moved, leading to the distortion of crystal lattice. A major distortion of lattice leads to increase the resistance of carbon atoms migration. The Ni(100) lattice presents nonsymmetrical distortion when the carbon atoms migrate between the gaps. The lattice distortion in different directions is inconsistent, which further increases the distortion energy. Thereby, the solubility limit of carbon atoms in nickel is

![Fig. 8. The number of reactant over time.](image)

![Fig. 9. The migration path of carbon atoms in the matrix.](image)
reduced. Thus, the driving force of diffusion in the initial stage is because of concentration difference of carbon atoms and the carbon atoms diffuse from high concentration gap to lower one. The macroscopic diffusion of carbon in nickel will decrease quickly when the concentration field of carbon atoms in Ni(100) turn to a homogeneous phase. Therefore, improving the stability of the Ni–C bond can make carbon atoms difficult to diffuse into the nickel lattice. Therefore, the way of using the mixed impurity elements to form a particular nickel solid solution can reduce the stability of Ni–C, which is able to improve the stability of the structure of nickel.

Although, the atom transfer resistance caused by lattice distortion can reduce atomic migration rate and even block this process, as the Fig. 6 shows, the carbon atom content of the system still presents gradually increase at the later period during carbon atoms migration process. This is because the real driving force in carbon migration process is the chemical potential caused by uneven distribution of carbon atoms. The carbon atoms migrate from area of high chemical potential to low chemical potential. When the chemical potential of the system tends to be balance, the carbon atoms macroscopic diffusion stops, and some Ni–C bonds breakage leads to formation of C–C bonds in the solid solution. The C–C bond has high chemical stability and which forms carbon chain. With the accumulation of carbon atoms, the carbon clusters are formed and then phase inversion takes place (see Fig. 10). Therefore, when driving force starts to decrease during concentration diffusion process, a new driving force comes out for carbon migration due to the formation of new phase. Consequently, carbon migration process is changed from concentration diffusion to uphill diffusion.

The carbon atoms gradually dissolve into the Ni(100) during the process of adsorption and migration, leading to the crystallization. In the process of crystal transition, the crystal lattice will distort, and new phase is formed in the solid solution. This inevitably leads to a reconstruction of Ni(100) structure and increase in internal stress. At the same time, the change in the basic structure will cause volume changes in different directions, which results in crystal fracture. When the amount of dissolved carbon atoms in the solid solution reaches a certain concentration, the carbon clusters accumulate in the interior (see Fig. 10) or form carbon fiber on the surface of nickel, leading to the structural damage of the SOFC anode and the formation of “metal dust” and the collapse of catalyst carrier and the active channel. The volume expansion of nickel in long-term operation of SOFC indicates that carbon deposition is mainly due to the migration of carbon atoms on the surface of nickel and enrichment on the surface [28,29]. However, the volume expansion of nickel in this study is not only carburing, but also the rupture of nickel causes the carbon to have more migration channels. An effective way to reduce coke is to minimize the contact possibility between the carbon and nickel atoms. For example, we can use inertia elements to modify the nickel surface, which can effectively influence the steric hindrance in the carbon adsorption process [31]. The Simulation using ReaxFF-MD helped in understanding the process of coke formation on anode. This method can be utilized to further investigate the reduction in coke formation by studying numerous nanostructured interfaces on the nickel surface to increase the steric hindrance for carbon adsorption process.

4. Conclusions

This paper demonstrated the adsorption mechanism of methane, methanol and ethanol on Ni(100) surface and the diffusion process of carbon atoms in Ni(100). Fig. 10 clearly illustrates the coke formation progress and influences on the nickel-based anode of SOFC. The Simulation using ReaxFF-MD clearly shows the process of coke formation on anode. It was found that the diffusion process could be divided into three steps, adsorption, diffusion and re-adsorption. The alkyl was more easily adsorbed on the surface in adsorption step. At the diffusion stage, the driving force of carbon atoms in Ni(100) changes because of forming new phase of carbon cluster at the later stage which leads to the damage of Ni(100). Finally, in re-adsorption more carbon atoms attached to the surface, resulting in minimized reforming process. The coke in anode can be effectively reduced by controlling the adsorption rate at the first place and slow down the carbon atom’s adsorption and diffusion progress by doping other elements on the nickel surface to increase the steric hindrance of carbon adsorption process. This method can be utilized to further investigate the reduction in coke formation by studying numerous nanostructured interfaces on the nickel surface. This will not impede the charge transfer process across the interfaces and allow achieving high-power output by using higher-order hydrocarbons.

Fig. 10. The mechanisms of coke formation and mechanical damage mechanism of the anode.
i. The reforming reaction process; ii. Carbon deposition forming process; iii. TEM images of carbon fibers and graphite carbon [22]; iv. Carbon atoms migration process; v. Internal stress caused by the formation of new phase; vi. Carbon clusters in Model-1@ 500 ps, 2000 K.