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# Improvement of hydrogen isotope exchange reactions on $Li_4SiO_4$ ceramic pebble by catalytic metals

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**Abstract**

$Li_4SiO_4$ ceramic pebble is considered as a candidate tritium breeding material of Chinese Helium Cooled Solid Breeder Test Blanket Module (CH HCSB TBM) for the International Thermonuclear Experimental Reactor (ITER). In this paper, $Li_4SiO_4$ ceramic pebbles deposited with catalytic metals, including Pt, Pd, Ru and Ir, were prepared by wet impregnation method. The metal particles on $Li_4SiO_4$ pebble exhibit a good promotion of hydrogen isotope exchange reactions in $H_2$–$D_2O$ gas system, with conversion equilibrium temperature reduction of 200–300 °C. The out-of-pile tritium release experiments were performed using 1.0 wt% Pt/$Li_4SiO_4$ and $Li_4SiO_4$ pebbles irradiated in a thermal neutron reactor. The thermal desorption spectroscopy shows that Pt was effective to increase the tritium release rate at lower temperatures, and the ratio of tritium molecule (HT) to tritiated water (HTO) of 1.0 wt% Pt/$Li_4SiO_4$ was much more than that of $Li_4SiO_4$, which released mainly as HTO. Thus, catalytic metals deposited on $Li_4SiO_4$ pebble may help to accelerate the recovery of bred tritium particularly in low temperature region, and increase the tritium molecule form released from the tritium breeding materials.


*Keywords:* Lithium orthosilicate ($Li_4SiO_4$); Hydrogen isotope exchange reaction; Catalytic metal; Tritium

Lithium-containing ceramics, such as $Li_2O$, $LiAlO_2$, $Li_2ZrO_3$, $Li_2TiO_3$ and $Li_4SiO_4$, are considered as tritium breeding materials to sustain the D–T fusion reaction in a fusion reactor [1,2]. Tritium is produced *via* $^6Li(n,\alpha)T$ in the lithium-containing ceramics, and extracted from the solid surface by a helium sweep gas with a fraction of hydrogen or deuterium. Considering to reduce the residence time of tritium in the breeder blankets, the bred tritium must be carried out at a fast recovery rate over a broad range of temperature, so some means shall be developed.

The mass transfer mechanism of tritium released from the lithium-containing ceramics is developed and assumed commonly that tritium is bred in grain interior, diffuses to the surface layer, and transfers to the surface water. Finally, tritium at the surface water discharges to the purge gas through surface reactions [3]. However, the isotope exchange reactions at the interface between solid surface and sweep gas are very slow at low temperatures, only fast at relatively elevated temperatures (>700 °C) [4,5]. If the isotope exchange reactions contribute strongly to the tritium release rate,

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a large number of tritium will remain in the breeding materials. Then platinum and palladium were tried to deposit on lithium-containing ceramics to accelerate the isotope exchange reaction rate at low temperatures [4–6]. Considering the practical application of neutron activity materials in a fusion reactor, many problems need systematic study, such as comparison of different catalytic metals, the optimization of metal content and catalyst poisoning.

In order to search some ways to enhance the tritium release in CH HCSB TBM, $Li_4SiO_4$ ceramic pebbles deposited with four kinds of catalytic metals were prepared in this paper. The effects of different metals deposited and Pt content on the hydrogen isotope exchange reactions were examined and compared in a $H_2/D_2O$ gas system. The tritium release behaviors of the neutron-irradiated 1.0 wt% $Pt/Li_4SiO_4$ and $Li_4SiO_4$ were studied through the out-of-pile tritium release experiments.

## 1. Experimental

$Li_4SiO_4$ ceramic pebbles were prepared by freeze-sintering process [7]. $Li_4SiO_4$ ceramic pebbles (av. 0.9 mm in diameter) were selected to be deposited with noble metals by wet impregnation method as follows. The pebbles were dried in a vacuum drier at 150 °C for 3 h. Then the metal-containing water solution, containing $H_2PtCl_6$, $H_2IrCl_6$, $PdCl_2$ or $RuCl_3$, was dripped on the pebbles, and adsorbed swiftly by the pebbles. When the pebbles were saturated with the solution, they were dried for 1–2 h by infrared ray. After repeating the above steps until the pebbles had adsorbed the predetermined amount of metal, they were deoxidized in a 5 vol% $H_2/N_2$ mixture gas at 400–450 °C for 3 h. Finally $Li_4SiO_4$ ceramic pebbles with catalyst were obtained.

A settled reactor ($\phi$ = 8 mm) apparatus was used to study the hydrogen isotope exchange behavior on the surface of $Li_4SiO_4$ ceramic pebble. The samples were dried at 150 °C for 2 h in a vacuum drier, and then installed in the reactor. A mixture gas of helium containing $H_2$ (1080 ppm) and $D_2O$ (1120 ppm) was introduced into the reactor. The concentration of $D_2O$ was controlled by gas passing through a CuO bed of 350 °C. The deuterium concentration in the outlet stream of the reactor was measured by a gas chromatogram (Agilent 6890N).

Out-of-pile tritium release experiments have been performed using the temperature programmed desorption technique. $Li_4SiO_4$ and 1.0 wt% $Pt/Li_4SiO_4$ ceramic pebbles were sealed in quartz capsules and irradiated in a thermal neutron reactor with a neutron flux of $7.1 \times 10^{12}$ $cm^{-2}$ $s^{-1}$ for 100 min at ambient temperature (29–36 °C). After irradiation, the samples were placed at room temperature for about two years. The quartz capsules were broken in a glove bag full of He gas, and some pebbles about 0.01–0.02 g were transferred into a reactor tube made of quartz for the tritium release experiment. The reactor tube was heated at a heating rate of 5 °C $min^{-1}$ from room temperature to 800 °C, while a purge gas of He containing 1 vol% $H_2$ carried the released tritium (HT and HTO) through the experimental system at a flow rate of 50 mL $min^{-1}$. Two ionization chambers were used to measure the total tritium (HTO&HT) and HT respectively. HTO was measured by a liquid scintillation counting equipment.

Fig. 1. Photo images of 1.0 wt% $Pt/Li_4SiO_4$ pebble.