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TNO report

CATO-D2.3.5&6&7

Final report project results related to high temperature oxygen generation (CATO Deliverable 2.3.7, incl. D-2.3.5 & D2.3.6)

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Public Summary

The investigation of high temperature oxygen generation materials was carried out as combined effort within the EU project ENCAP (SP5) and CATO. The research was performed in close cooperation with BOC, Linde, Statoil, Sintef and the University Twente. This report focuses on the results that can be related to the Dutch interest.

In the period March 2004-August 2005, TNO Science and Industry (S&I) was active in the development of new high temperature oxygen generation materials and the performance-stability relationship properties of oxygen sorption materials (CAR (Ceramic Auto thermal Recovery)-process materials) and membrane materials at relevant process conditions [1]. In September 2005 the partners of SP5 selected the CAR process as the most promising process and the research was focussed on only high temperature oxygen generation materials for the CAR process.

In the period between September 2005 and August 2006 BOC-2, BOC-10, BOC-10c BOC-11 and BOC-12 were tested on their stability for application in the CAR-process. At SINTEF SASRA (Simulated Ambient Steam Reforming Analysis) and re-oxidation/restoration experiments were performed on these samples. The SASRA experiments were performed at 750, 850 and 950°C in a stream of 1:2 molar CO_2+H_2O gas mixtures at total pressure of 1 bar for 1 week. For the 950°C measurements SINTEF rebuilt the SASRA set-up. The restoration experiments were performed on SASRA treated samples at 750, 850 and 950 °C in air for 60 h. At TNO the fresh, SASRA and re-oxidized samples were characterized by XRD (X-ray diffraction).

BOC-2 ($La_xSr_yCo_zFe_mO_n$) has the highest stability for application in the CAR process. In the temperature range of 650-850 °C BOC-2 is almost stable, at 950 °C BOC-2 degrade partly into $SrCoO_x$. After the SASRA treatment at 750 and 850 °C only small changes appear in the structure, due to the reduction of Co/loss of oxygen and/or the degradation of BOC-2 to $Sr_2Fe_2O_5$. After re-oxidation at 650-950 ˚C the structures of fresh BOC-2 samples and of the reoxidized BOC samples appeared to be very similar.

BOC-10, BOC-11 and BOC-12 are less stable than BOC-2 during SASRA treatment. After SASRA treatment BOC-10, BOC-11 and BOC-12 contain the degrade products of $SrCoO_3$ (2θ= 25,2˚) and $Sr_qCo_pO_n$ (2θ= 28,5˚). The amount of degrade $SrCoO_3$ (peak area) is in the samples BOC-10, BOC-11 and BOC-12 approximately the same. At re-oxidation temperatures of 950 ˚C all the material could reactivate mainly to the original composition without large amounts of degradation products. BOC-2 could be reoxidised and reactivated in the temperature range 650-950 ˚C, BOC-10 and BOC-12 could be reoxidised and reactivated in the temperature range 850-950 ˚C, BOC-11 could be reoxidised at 950 ˚C. The amount of $Sr_2Co_2O_5$ (peak area) after reoxidation at 650 and 750 °C is increasing from BOC-10, BOC-12 to BOC-11.

The stability order based on the SASRA/XRD experiments presented in this memo is: BOC-2 >>BOC-10>BOC-12>BOC-11. These results are in agreement with the CAR-measurements performed at BOC. [4]. The structure of “fresh” BOC-10c (commercial) is not the same as “fresh” BOC-10 (obtained from BOC). The stability/degradation behaviour during SASRA treatment and re-oxidation are for BOC-10 and BOC-10c the same.
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