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Article

$Ce_{0.67}Cr_{0.33}O_{2.11}$: A New Low-Temperature O_2 Evolution Material and H_2 Generation Catalyst by Thermochemical Splitting of Water[†]

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$Ce_{0.67}Cr_{0.33}O_{2.11}$ was synthesized by hydrothermal method using diethylenetriamine as complexing agent (*Chem. Mater.* **2008**, *20*, 7268). $Ce_{0.67}Cr_{0.33}O_{2.11}$ being the only compound likes $UO_{2+\delta}$ to have excess oxygen, it releases a large proportion of its lattice oxygen (0.167 M [O]/mole of compound) at relatively low temperature (465 °C) directly and it has been utilized for generation of H_2 by thermo-splitting of water. An almost stoichiometric amount of H_2 (0.152 M/Mole of compound) is generated at much lower temperature (65 °C). There is an almost comparable amount of oxygen release and hydrogen generation over this material at very low temperature compared to other CeO_2-MO_x (Mn, Fe, Cu, and Ni) mixed-oxide solid solutions (O_2 evolution $\geq$1300 °C and H_2 generation at 1000 °C). The reversible nature of oxygen release and intake of this material is attributed to its fluorite structure and coupling between the Ce^{4+}/Ce^{3+} and $Cr^{4+/6+}/Cr^{3+}$ redox couples. Compound shows reversible oxygen release and intake by H_2O absorption and subsequent hydrogen release to gain parent structure and hence this material can be utilized for generation of H_2 at very low temperature by thermo-chemical splitting of water.

Introduction

The utilization of hydrogen (H_2) energy as a clean energy is a solution to solve global environmental problems and exhaustion of natural energy resources. Water is the most abundant molecular compound on Earth: it is omnipresent and essential for life. Water is a stable compound because of its high formation enthalpy of -286 kJ mol^{-1}, and thus the splitting of water in to H_2 and O_2 is a high-energy process. The thermal splitting of water requires temperatures above 2500 °C. In the theromchemical process, hydrogen is generated at a lower temperature by involving different chemical reactions than the direct thermal decomposition of water in to H_2 and O_2. One of the simplest examples of such a cycle is generation of H_2 by two-step water splitting involving the metal oxide redox pair in the thermochemical cycle.[1−3] They can be represented as follows.

Oxygen releasing step

$$MO_{ox} \rightarrow MO_{red} + 1/2O_2 \qquad (1)$$

H_2 generation step

$$MO_{red} + H_2O \rightarrow MO_{ox} + H_2 \qquad (2)$$

Redox systems of FeO/Fe_3O_4, CoO/Co_3O_4, MnO/Mn_3O_4, Zn/ZnO have been studied for two-step water splitting.[2−5] A cerium oxide process has been reported by Abanades and Flamant.[6] The process uses a CeO_2/Ce_2O_3 redox pair and reaction occurs in two step process as follows

$$2CeO_2(s) \rightarrow Ce_2O_3(s) + 1/2O_2(g) \quad 2000°C \qquad (3)$$

$$Ce_2O_3(s) + H_2O(g) \rightarrow 2CeO_2(s) + H_2(g) \quad 400-600°C \qquad (4)$$

The amount of lattice oxygen that can be reversibly exchanged from CeO_2 is called oxygen storage capacity.[7,8] CeO_2 is a fantastic material utilized in exhaust catalysis because of its oxygen storage capacity (OSC). Substitutions of other transition metal ion in CeO_2 are shown to enhance the OSC of $Ce_{1-x}M_xO_2$ (Zr, Ti).[9−13] It means lattice oxygen is activated and can be removed

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relatively easily. So substitution of other transition metal will not only enhance the OSC but can also bring down the oxygen releasing temperature. Indeed CeO_2-MOx (M = Mn, Fe, Cu, and Ni) mixed oxide solid solutions have shown higher amount of oxygen release at relatively low temperature (1400 °C) than CeO_2 and their subsequent utilization for generation of hydrogen from water splitting at lower temperature.[14]

In our efforts to search for new high OSC materials for exhaust catalysis we have developed OSC materials such as $Ce_{1-x}Ti_xO_2$ ($0 \leq x \leq 0.40$),[12] $Ce_{1-x}Sn_xO_2$ ($0\leq x \leq 0.50$),[15] $Ce_{1-x}Cr_xO_{2.11}$ ($0 \leq x \leq 0.33$),[16] which have shown very high OSC at lower temperature. Among these OSC materials, $Ce_{0.67}Cr_{0.33}O_{2+\delta}$ not only has shown higher OSC capacity than $Ce_{0.5}Zr_{0.5}O_2$ but it also releases lattice oxygen directly at much lower temperature (~300 °C).[16] In this paper, we report the study of O_2 evolution and the generation of H_2 by thermochemical splitting of water over $Ce_{0.67}Cr_{0.33}O_{2.11}$ catalyst. Oxygen release starts around 300 °C from $Ce_{0.67}Cr_{0.33}O_{2.11}$ but for higher O_2 release and taking the stability of the material into account as well, we studied oxygen release at 465 °C and H_2 generation from water splitting starts at as low a temperature as 65 °C over this material.

Experimental Section

$Ce_{0.67}Cr_{0.33}O_{2.11}$ was synthesized by hydrothermal method represented in our earlier work.[16] In a typical synthesis, 6.7 mM $Ce(NH_4)_2(NO_3)_6$ was dissolved in 20 mL of water and 3.3 mM CrO_3 was dissolved in 15 mL of water. Both the solutions were mixed, and 0.03 M (3.1 mL) of diethylenetriamine was added. The resulting dark yellow colored gel formed was transferred in three autoclave bomb of 20 mL size with 75% of filling. The autoclave bombs were heated at 200 °C for 24 h in a hot air oven. After reaction resulting solid was centrifuged and dried at 110 °C. The solid product was characterized by powder X-ray diffraction (XRD). X-ray diffraction patterns of all samples were recorded in a Phillips X'Pert diffractometer using Cu Kα radiation at scan rate of 0.25° min^{-1} with 0.01° step size in the 2θ range between 10 and 90°. Structures were refined by Rietveld method, using FullProf-fp2k program.[17]

Composition is also confirmed by energy-dispersive X-ray (EDX) analysis (JEOL JSM 5600LV scanning electron microscope). To know the oxidation states of the elements in the compound, we recorded X-ray photoelectron spectra (XPS) on a Thermoscientific Multilab 2000 equipment employing Al Kα X-rays at 150W. XPS binding energies are accurate within ±0.1 eV. A thermogravimetric (TG) analysis was carried out on a home-built apparatus in air in the temperature range 30−500 °C at a heating rate of 4 °C/min.

Oxygen evolution and hydrogen generation experiments were done in a micro reactor of length 30 and 0.4 cm internal diameter with ultra high pure (UHP) N_2 (certified calibration gas mixture from Bhoruka gases Ltd., India) flowing at 100 sccm. Oxygen evolution experiments were done over 350 mg of compound by heating it at 465 °C for 1 h and hydrogen generation experiments were done by cooling the sample to 50 °C in water vapor along with N_2. The flow of water vapor was then stopped and the sample was heated in UHP N_2 at 65 °C to release hydrogen. The generated oxygen and hydrogen gases were analyzed by gas chromatograph (GC). Total amount of hydrogen generated is also measured gravimetrically by passing the generated hydrogen over CuO at 300 °C. The amount of hydrogen is calculated from the weight loss of CuO because of its reduction to Cu by H_2 generated through water splitting.

Result and discussion

The powder XRD pattern of as prepared $Ce_{0.67}Cr_{0.33}O_{2.11}$ is shown in Figure 1(a). Powder X-ray pattern is indexed to fluorite structure. The Rietveld refined XRD profile of $Ce_{0.67}Cr0.33O_{2.11}$ is shown in Figure 2. Structural parameters of $Ce_{0.67}Cr_{0.33}O_{2.11}$ obtained by Rietveld refinement of powder XRD data are summarized in Table 1. Thermal stability of compound is studied by heating the compound in furnace at different temperature. The compound is stable up to 550 °C. Powder XRD pattern of sample heated at 550 °C is shown in Figure 1(b) and no diffraction lines were observed either for Cr_2O_3, CrO_2, or Cr metal in powder XRD pattern. But when heated at 600 °C for 2 h, impurity peaks for Cr_2O_3 are observed in the powder XRD pattern (not shown).

Structure, composition, oxygen storage capacity and oxygen evolution have been described in details in our previous work.[16] $Ce_{0.67}Cr_{0.33}O_{2.11}$ shows high oxygen

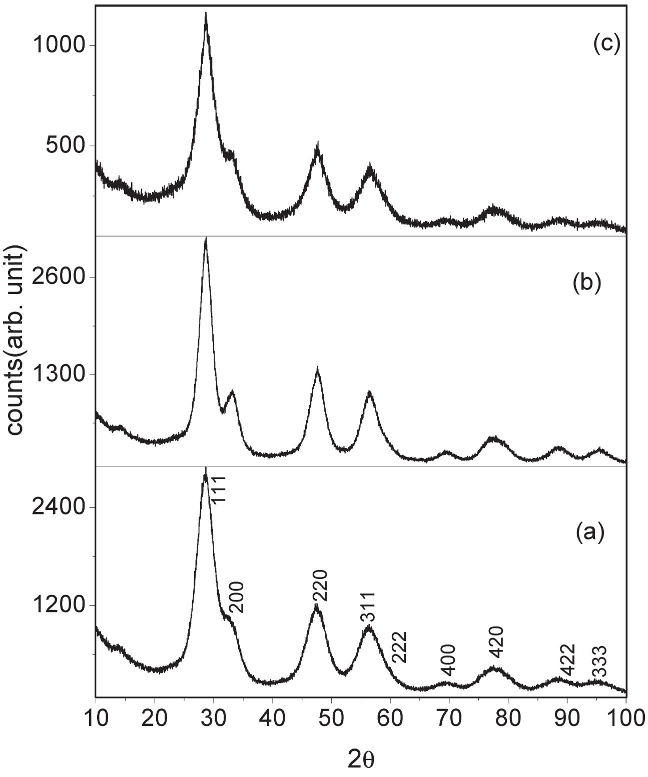

Figure 1. Powder XRD pattern of (a) $Ce_{0.67}Cr_{0.33}O_{2.11}$ as-prepared, (b) $Ce_{0.67}Cr_{0.33}O_{2.11}$ heated to 550 °C, and (c) $Ce_{0.67}Cr_{0.33}O_{2.11}$ after 8 cycles of H_2 generation.

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storage capacity and oxygen release by heating in air. The compound ($Ce_{2/3}Cr_{1/3}O_{2.11}$) was heated under flow of He and gaseous products were analyzed by means of a quadrupole mass spectrometer. There were no additional peaks observed except O_2 evolution with M/e at 32 was indeed observed, which was increasing with increasing temperature. O_2 evolution plot is given in our earlier paper.[16] Oxygen evolution in this material starts around 200 °C. To see the nature and the amount of oxygen evolution, TGA of the sample is done in UHP N_2. From the TG curve in Figure 3, it is clear that weight loss is continuous after 200 °C, a small plateau is found around 450 °C, and then fast weight loss is observed. The weight loss is around 1.1% up to 450 °C, which is equivalent to 0.1 mol of [O]. From TGA plot, the total weight loss up to 550 °C is 3.1%, which corresponds to 0.28 mol of O/mol of compound. We have chosen oxygen removal experiment at 465 °C because weight loss is fast after 450 °C and the compound is also stable at this temperature. The schematic diagram of experimental set up for O_2 release and H_2 generation experiment is shown in Figure 4. Oxygen release experiment is done by heating the sample in UHP N_2 at 465 °C until O_2 evolution is observed in a GC. The amount of evolved oxygen is calculated by calibrating the GC signal for evolved oxygen signal against the oxygen signal for known composition of O_2 in N_2. The oxygen evolution plot is shown for three cycles in Figure 5a−c.

By taking 144.8 as the molecular weight of compound $Ce_{0.67}Cr_{0.33}O_{2.11}$, the amount of [O] released are 0.148, 0.186, and 0.163 M [O]/mol of oxide, respectively, for first, third, and fifth cycles. Average oxygen release with six consecutive cycles is 0.167 mol of O/mol of oxide. Values for each cycle are given in table 2. For H_2 generation, compound is heated in a N_2 flow at 465 °C until oxygen evolution stops completely. Water vapor is passed along with N_2 and compound is cooled up to 50 °C under water vapor but no H_2 signal is detected, we stopped the water vapor flow and under N_2 flow only we heated the compound at 65 °C and hydrogen evolution was observed. Compound is heated at this temperature until the H_2 signal stopped. The H_2 signal observed after stopping the water vapor flow and heating under N_2 only because in the presence of high partial pressure of H_2O vapor, H_2O dissociation does not occur; similarly, no H_2 detection/release is observed when water vapor is passed at higher temperature (∼450 °C). As seen from TGA, the rate of oxygen evolution is highest around 450 °C. Therefore, material can not be oxidized by O_2 or H_2O at this temperature at atmospheric pressure. The compound starts losing weight by heating in air and weight loss starts around 200 °C[16] When the compound is cooled below the oxygen desorption temperature, oxidation is expected. That is why we need to cool the compound

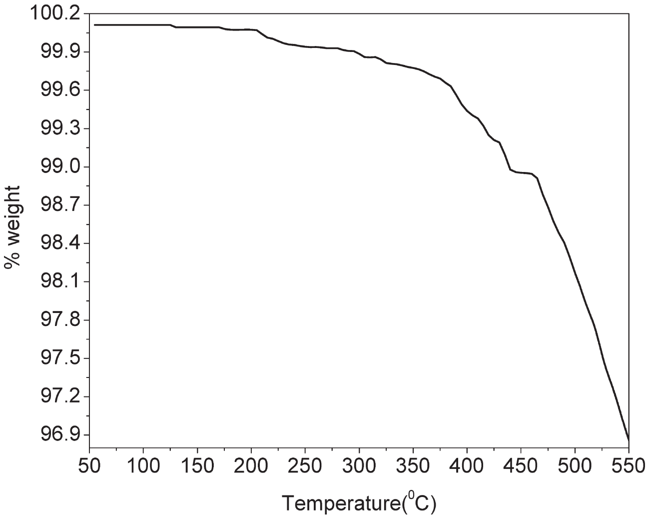

Figure 3. Thrmogravimetry (TG) curve of $Ce_{0.67}Cr_{0.33}O_{2.11}$ under a N_2 flow.

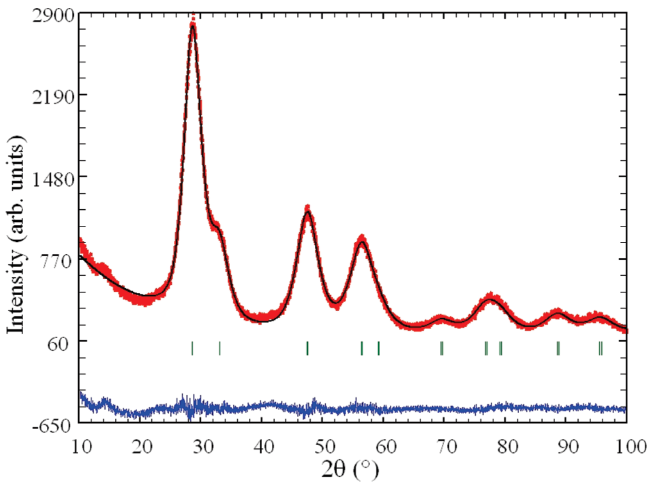

Figure 2. Rietveld refined powder XRD profile of as-prepared $Ce_{0.67}Cr_{0.33}O_{2.11}$.

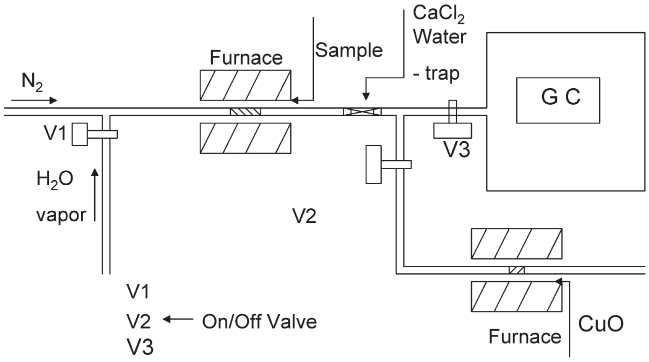

Figure 4. Schematic diagram of O_2 evolution and H_2 generation set up.

Table 1. Structural Details of $Ce_{0.67}Cr_{0.33}O_{2.11}$ at Various Reaction Conditions

compd	condition	lattice parameter	χ^2	R_B	R_f
$Ce_{0.67}Cr_{0.33}O_{2.11}$	as-prepared	5.352(2)	1.37	0.39	0.30
$Ce_{0.67}Cr_{0.33}O_{2.11}$	heated up to 550 °C	5.369(3)	0.88	1.41	0.72
$Ce_{0.67}Cr_{0.33}O_{2.11}$	After 8 cycle of hydrogen generation	5.375 (2)	0.87	0.64	0.41

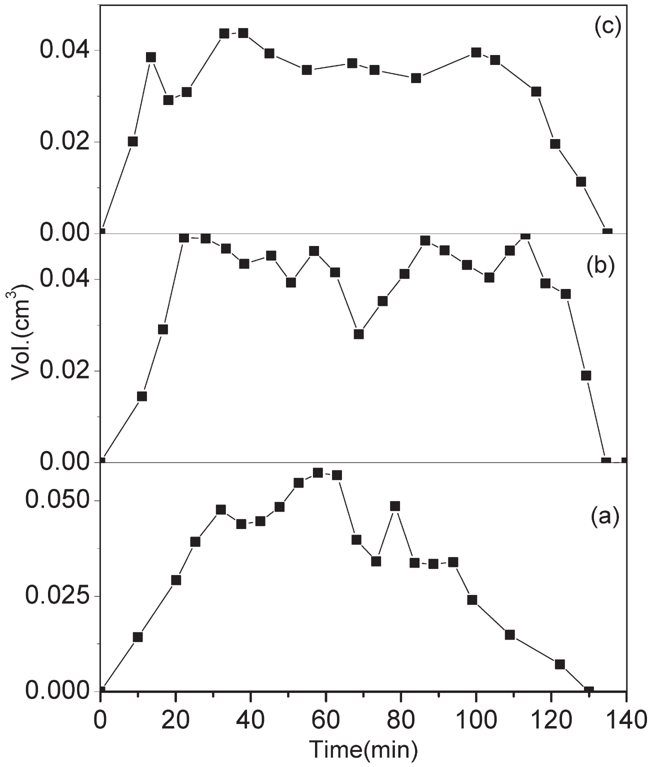

Figure 5. O_2 evolution curve for (a−c) 1st, 3rd, and 5th cycles, respectively, by heating the material at 465 °C under a N_2 flow.

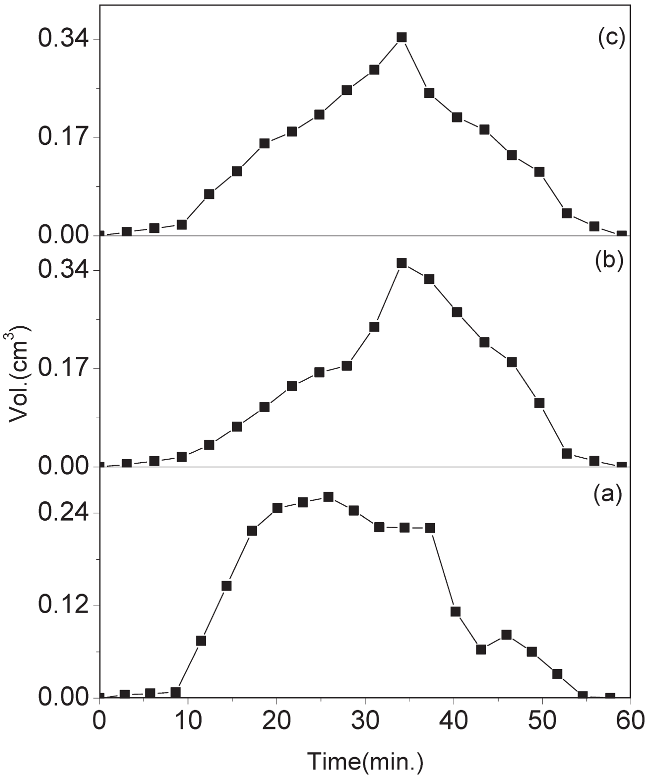

Figure 6. H_2 evolution curve for (a−c) 1st, 3rd, and 5th cycles, respectively, by heating the material at 65 °C under a N_2 flow.

Table 2. Details of Oxygen Evolution and Hydrogen Gneration over $Ce_{0.67}Cr_{0.33}O_{2.11}$

cycle no.	amount of O in mM/mol of compound generated at 465 °C (GC estimation)	amount of hydrogen in mM/mol of compound generated at 65 °C	
		from GC estimation	from gravimetric estimation
1	0.148	0.133	
2	0.171	0.147	
3	0186	0.146	
4	0.172	0.151	
5	0.163	0152	
6	0.165	0.153	
7	0.167		0.18
8	0.166		0.18

below 100 °C. O_2 is released from pure CeO_2 at 2000 °C and for CeO_2-MO_x (M = Fe, Mn, Cu, and Ni) is around 1300−1500 °C and the reduced compound is reoxidized at lower temperature ~500 °C by water.[6,14] By the substitution of $Cr^{4+/6+}$ ion in CeO_2, the oxygen evolution temperature is brought down to 465 °C and H_2 generation temperature at 65 °C.

The amount of evolved H_2 is calculated by calibrating the GC signal for evolved hydrogen signal against the H_2 signal for known composition of H_2 in N_2. The hydrogen generation plot is shown for three cycles in Figure 6a−c at 65 °C. By taking the molecular weight of the compound to be 144.8, the amount of H_2 generated is 0.133, 0.146, and 0.152 M H_2/mol of oxide in the first, third, and fifth cycles, respectively. The amount of H_2 generated in each cycle are given in Table 2. Evolved H_2 is also estimated gravimetrically by passing the generated hydrogen over a known weight of CuO in a reactor heated continuously at 300 °C. From the weight-loss of CuO, because of formation of Cu metal by the reduction with generated H_2, the amount of H_2 is calculated. Details of H_2 generated by gravimetric analysis are also given in Table 2. There is a good agreement in amount of generated H_2 estimated by GC experiment and estimated gravimetrically by CuO reduction to Cu. H_2 generation is repeated of for 8 cycle by heating the compound in N_2 until O_2 evolution stops and further cooling in H_2O vapor along with N_2 up to 50 °C then again heating at 65 °C in N_2 only. The hydrogen generation step was tried at a higher temperature also. The rate of H_2 generation was increasing with increasing the water splitting temperature, but the amount of H_2 generated was decreased; for example, at 120 °C, it was 0.16 and at 210 °C, it was 0.13 mol/mol of compound. This is because O_2 evolution starts around 200 °C in N_2 (Figure 3) from this material and it may reduce the reoxidation process.

After performing the hydrogen generation experiment for 8 cycles by first heating the compound to release O_2 and then passing water vapor to generate H_2, we recharacterized the compound by XRD and XPS. There was no impurity peak in the powder XRD pattern shown in Figure 1c and diffraction lines are to index to fluorite structure only. Rietveld refined powder XRD pattern is also shown in Figure 7. Details of structure parameters of material after H_2 generation cycle are given in Table 1. There is no significant variation in lattice parameters of the material before and after several cycling. Oxidation state of material is characterized by XPS. XPS spectra of Cr(2p) and Ce(3d) region of $Ce_{0.67}Cr_{0.33}O_{2.11}$ after

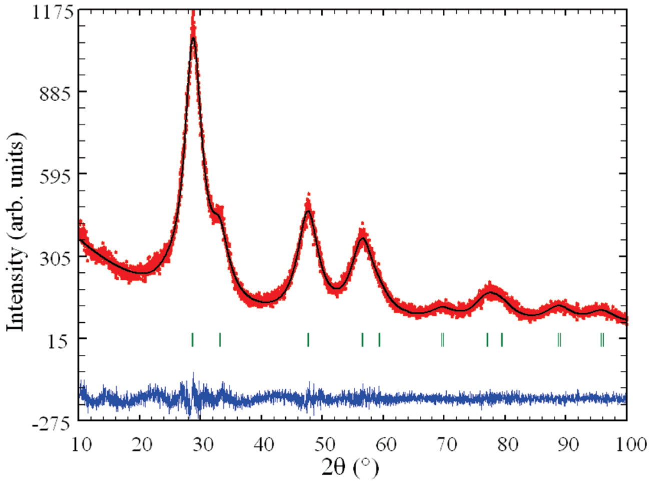

Figure 7. Rietveld refined powder XRD profile of $Ce_{0.67}Cr_{0.33}O_{2.11}$ after 8 cycles of H_2 generation.

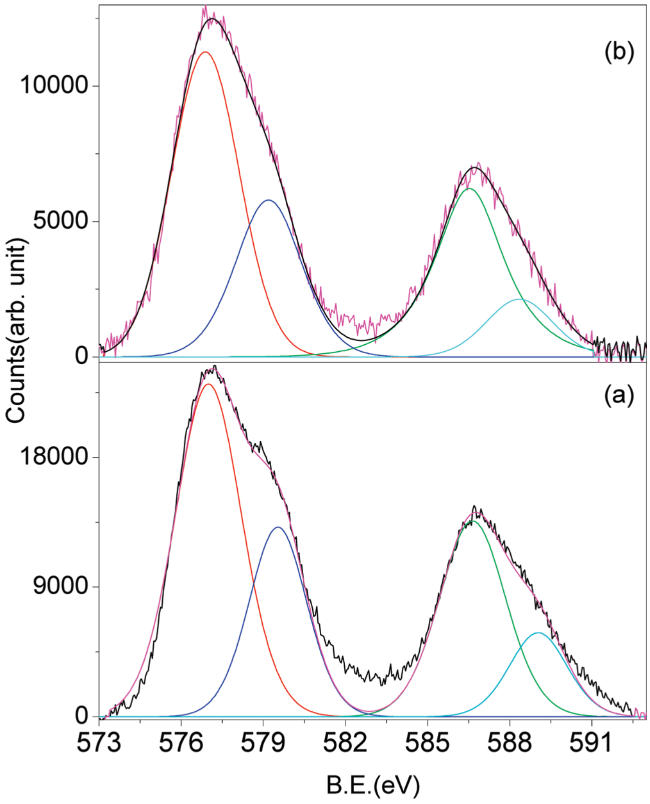

Figure 8. XPS of Cr(2p) region (a) $Ce_{0.67}Cr_{0.33}O_{2.11}$ after 8 cycles of H_2 generation and (b) $Ce_{0.67}Cr_{0.33}O_{2.11}$ before H_2 generation cycle.

8 cycles of H_2 generations is shown in Figures 8a and 9a, respectively. XPS of Cr(2p) and Ce(3d) region of as-prepared $Ce_{0.67}Cr_{0.33}O_{2.11}$ sample before cycling is also given for comparison in Figures 8b and 9b, respectively. There is no change in Cr (2p) spectra of the compound after hydrogen generation cycle as Cr exists in mixed-valence state $Cr(2p_{3/2})$(IV) and $Cr(2p_{3/2})$(VI) state in a ratio of ~2:1, only with B.E. at 576.9 and 579.3 eV, which matches with the as-prepared sample where Cr(2p) also exists in mixed (IV) and (VI) states with the ratio of ~2:1.[16] CrO_2 is a metallic oxide. Therefore, Cr(3d) electrons are delocalized. When a core hole ($Cr(2p^6)$ to $Cr(2p^5)+e$) is created due to photo ionization, electrons are transferred to the core hole by free electron in conduction band, unlike in the case of an insulating oxide such as Cr_2O_3. Therefore binding energy of $Cr^{4+}(2p_{3/2})$ at 576.3 eV in CrO_2[18] is lower than $Cr^{3+}(2p_{3/2})$ at 576.8 eV in

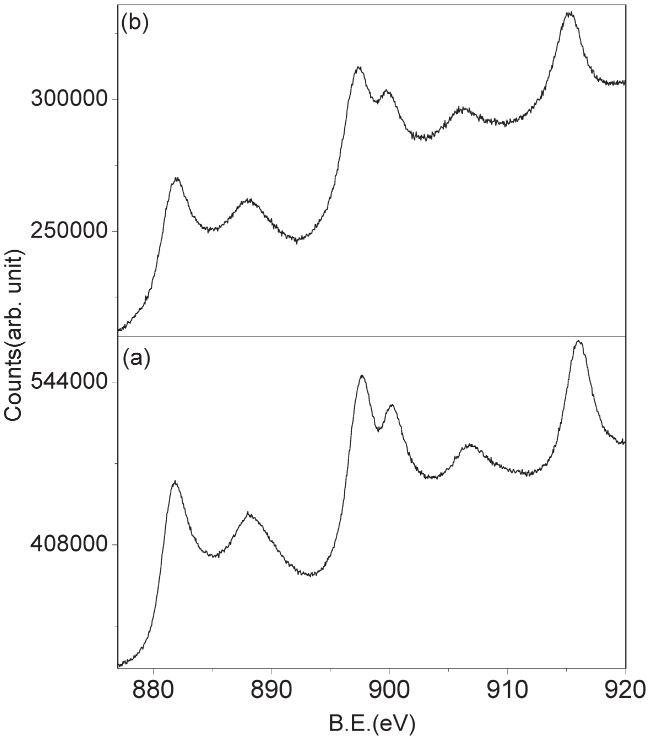

Figure 9. XPS of Ce(3d) region (a) $Ce_{0.67}Cr_{0.33}O_{2.11}$ after 8 cycles of H_2 generation and (b) $Ce_{0.67}Cr_{0.33}O_{2.11}$ before H_2 generation cycle.

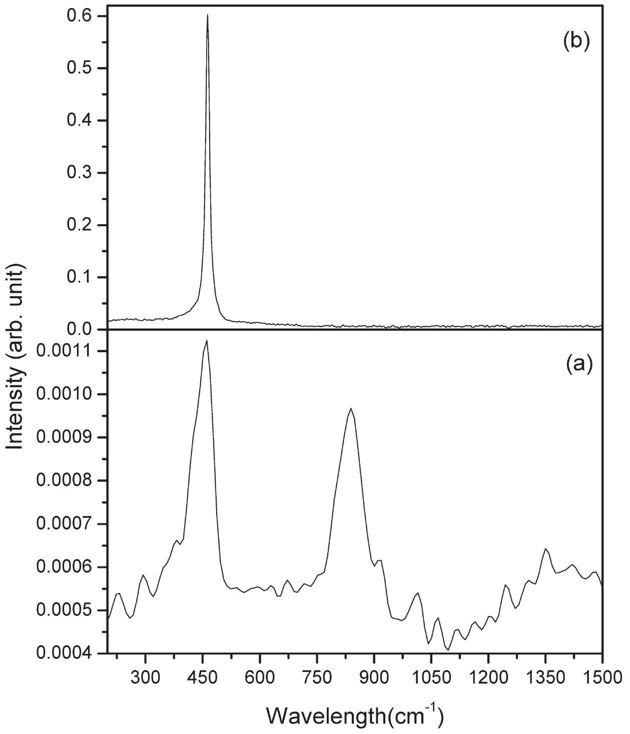

Figure 10. Raman spectra of (a) $Ce_{0.67}Cr_{0.33}O_{2.11}$ and (b) pure CeO_2.

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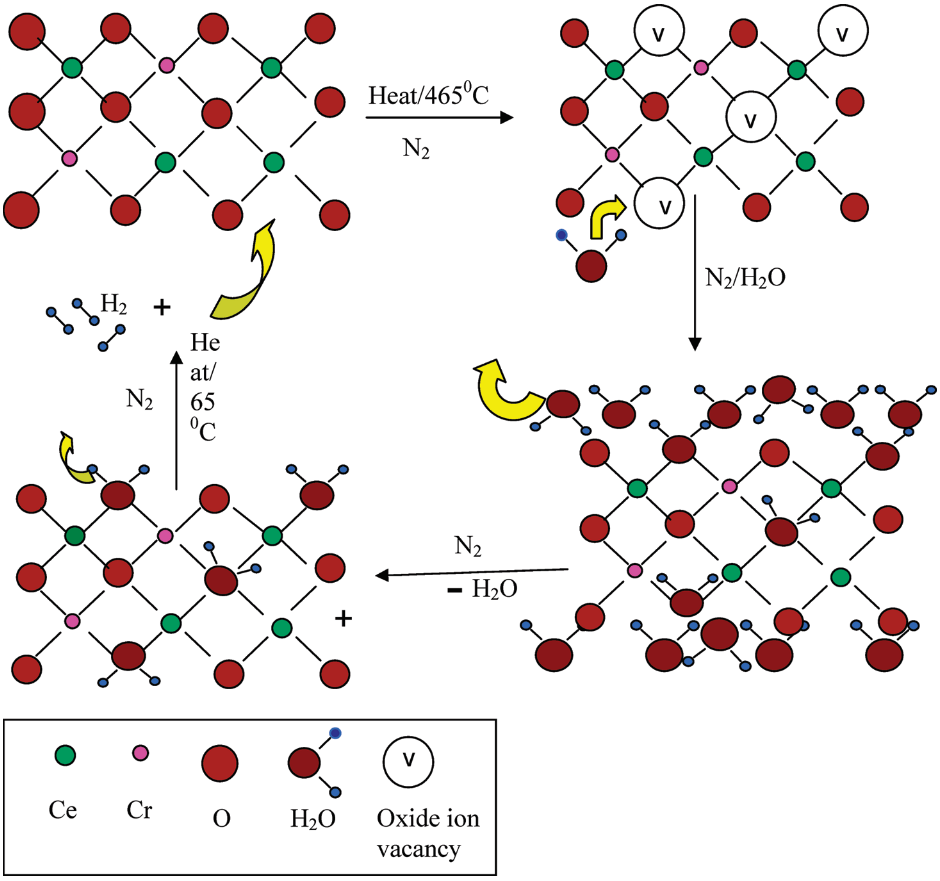

Figure 11. Representation of the mechanism of hydrogen generation.

Cr_2O_3.[19] Cr ion-substituted CeO_2 is not conducting. In fact, it is insulating and Cr ion is in an insulating environment as in Cr_2O_3 and therefore $Cr^{4+}(2p_{3/2})$ core level binding energy is higher that $Cr^{3+}(2p_{3/2})$ core level, which is actually observed. Binding energies for the Cr^{4+}-$(2p_{3/2})$ and $Cr^{6+}(2p_{3/2})$ state are observed at 576.9 and 579.3 eV and the $Cr^{6+}(2p_{3/2})$ binding energy is the same as in the CrO_4^{2-} ion in K_2CrO_4, which is also insulating. Further $Cr^{3+}(2p_{3/2})$ ion is observed at 576.4 eV in the H_2 reduced $Ce_{0.67}Cr_{0.33}O_{2.11}$ up to 550C. $Cr^{4+}(2p_{3/2})$ observed at 576.6 eV instead of 576.3 eV when CrO_2 film was grown over TiO_2 film, which is again a semiconductor.[20] So from XPS study presence of Cr ion in 4+ and 6+ state in $Ce_{0.67}Cr_{0.33}O_{2.11}$ is confirmed.

Further electronic state of Cr ion in $Ce_{0.67}Cr_{0.33}O_{2.11}$ is also investigated by Raman spectroscopy. Raman spectra of $Ce_{0.67}Cr_{0.33}O_{2.11}$ and pure CeO_2 are given in Figure 10 (a) and (b) respectively. Raman band at 462 cm-1 in Figure 10(a) is assigned as phonon mode stretching for symmetric breathing mode of oxygen atoms around cerium atom[21] and other band observed at 842 cm^{-1} in figure 10(a) is close to V_1 (A_g +$B_{2\ g}$) stretching band of CrO_4^{2-} at 853 cm^{-1} in K_2CrO_4[22] and (Cr−O−Cr) vibration for chromate ion.[23] There is no band observed at 543 cm^{-1}, which is characteristic band for Cr_2O_3.[24] So Raman spectroscopy study also reveals the absence of Cr^{3+} and presence of Cr^{6+} in $Ce_{0.67}Cr_{0.33}O_{2.11}$.Ce(3d) spectrum of the compound after hydrogen generation cycle also shows that Ce is only in 4+ state with Ce($3d_{5/2}$) at 881.8 eV and a characteristic satellite peak at 916.8 eV. There is no change in the compound either in crystal structure or in electronic structure after hydrogen generation cycles, showing the material is robust for H_2 generation and O_2 evolution. So with these details, the mechanism of H_2 generation is represented in Figure 11 and the reaction can be described as follows

$$\begin{tikzcd} Ce_{0.67}Cr_{0.33}O_{2.11} \arrow[r, "\text{heat}", "450^0C/2h"'] & Ce_{0.67}Cr_{0.33}O_{1.943} + 0.167[O] \arrow[d, "N_2/H_2O\text{ vapor}"] \\ & Ce_{0.67}Cr_{0.33}O_{1.943}(H_2O)_{0.167} \arrow[d, "N_2", "\text{Heat}/65^0C"'] \\ & Ce_{0.67}Cr_{0.33}O_{2.11} + 0.167\ H_2 \end{tikzcd}$$

In conclusion, 0.167 mol of [O] evolved at 465 °C from $Ce_{0.67}Cr_{0.33}O_{2.11}$ and corresponding H_2 generation at 65 °C.The amount of hydrogen generated is lower

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than pure CeO_2[6] and comparable to CeO_2-MO_x[14]. But oxygen release and H_2 formation temperature with $Ce_{0.67}Cr_{0.33}O_{2.11}$ are far lower than pure CeO_2[6] and CeO_2-MO_x[14]. So the oxygen evolution reaction can be written as

$$\begin{aligned}&Ce_{0.67}{}^{4+}Cr_{0.22}{}^{4+}Cr_{0.11}{}^{6+}O_{2.11}\\ &\rightarrow Ce_{0.67}{}^{4+}Cr_{0.216}{}^{4+}Cr_{0.114}{}^{3+}O_{1.943} + 0.167[O]\end{aligned}$$

Because of redox potentials of Ce^{IV}/Ce^{III} (1.61 V)[25] and Cr^{VI}/Cr^{III}(1.33 V),[25] Cr^{3+} will get oxidized by Ce^{4+} reduction and the reaction occurs as follows

$$3Ce^{4+} + Cr^{3+} \rightarrow 3Ce^{3+} + Cr^{6+}$$

and because in the fluorite the CeO_2 lattice Ce^{4+} exist in 8 coordination, Ce^{3+} in the fluorite lattice will be highly unstable and can get oxidized by O_2 or H_2O; the reaction can written as

$$2Ce^{3+} + H_2O \rightarrow 2Ce^{4+} + H_2 + O^{2-}$$

That is why compound shows reversible oxygen release and intake by H_2O absorption and subsequent hydrogen release to gain the parent structure and hence this material can not only act as very high oxygen release/storage material but also can be utilized for generation of H_2 by thermo-chemical splitting of water.

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