Supporting Information

Site selectivity of hydride in early transition metal Ruddlesden-Popper oxyhydrides

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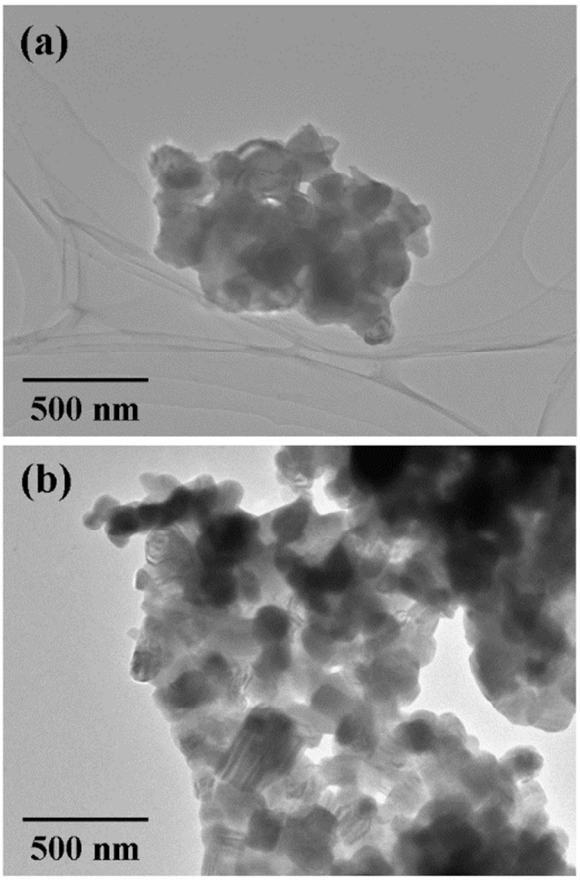

Figure S1. TEM images of (a) Sr_2TiO_4 and (b) $Sr_3Ti_2O_7$ precursors synthesized by the citrate method.

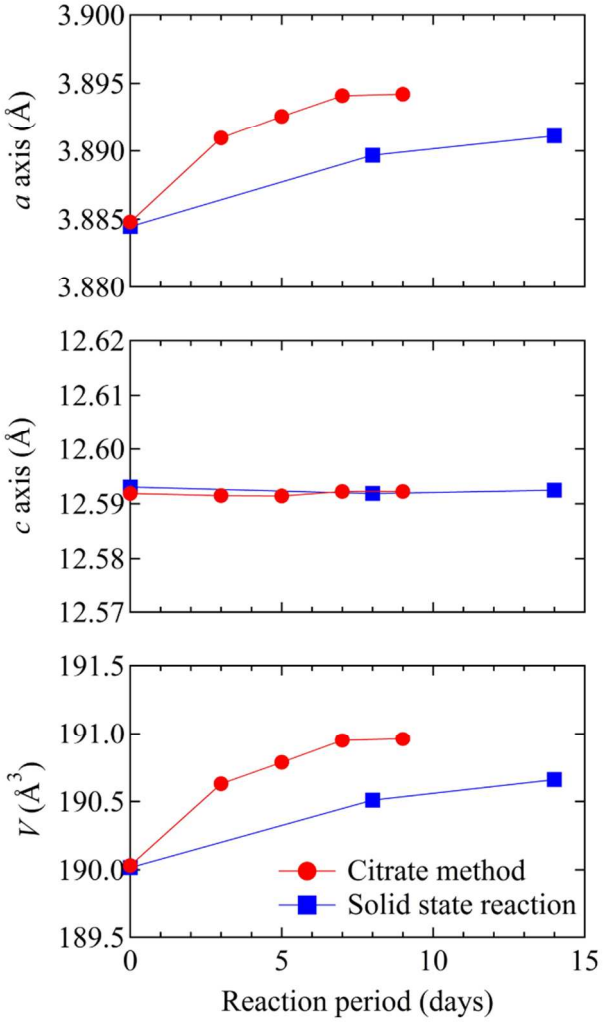

Figure S2.

Lattice parameters and cell volume (tetragonal symmetry) for starting material Sr_2TiO_4 and its reduced samples. In the analysis, three phases of $Sr_2TiO_{4-x}H_x$, $SrTiO_{3-y}H_y$ and TiH_2 are included. Both the starting materials synthesized by the citrate method and solid state reaction are shown here. The reduced samples are reacted with CaH_2 at 480 °C for various reaction periods. The error bars are generally within the size of the markers on the plot.

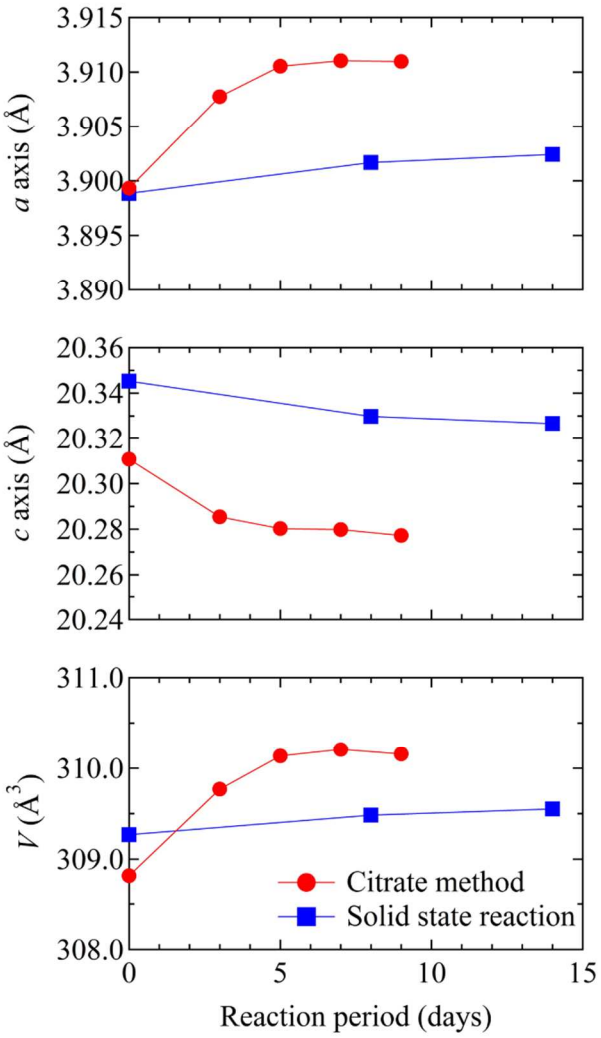

Figure S3. Lattice parameters and cell volume (tetragonal symmetry) for starting material $Sr_3Ti_2O_7$ and its reduced samples. Both the starting materials synthesized by the citrate method and solid state reaction are shown here. The reduced samples reacted with CaH_2 at 480 °C for various reaction periods. The error bars are generally within the size of the markers on the plot.

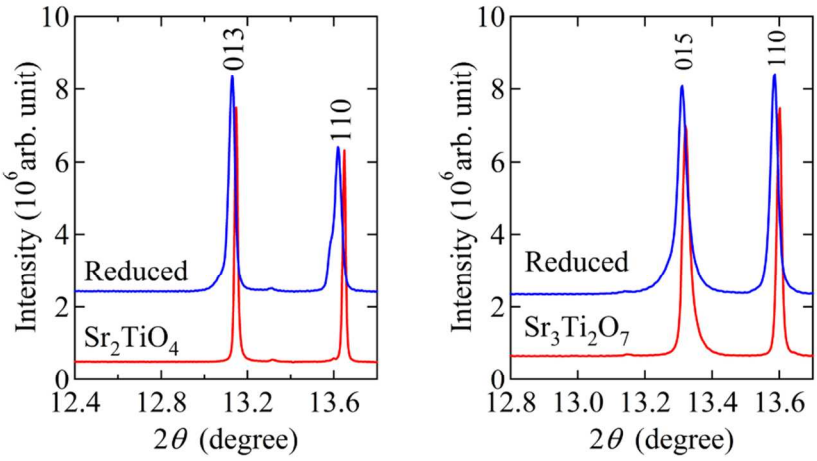

Figure S4. XRPD patterns for Sr_2TiO_4 and its reduced sample (left); for $Sr_3Ti_2O_7$ and its reduced sample (right). The starting materials were synthesized by solid state reaction. The reduced samples were reacted with CaH_2 at 480°C for 4 days. For reduced Sr_2TiO_4, Bragg peaks exhibit an asymmetric shape due to the presence of a shoulder on the left side (see *e.g.*, the (1 1 0) reflection). For reduced $Sr_3Ti_2O_7$ such a profile anomaly is not visible, reflection being simply symmetrically broadened with regard to the precursor material.

DFT calculations

I – Hydride ion and oxygen vacancy in Sr_2TiO_4 and $Sr_3Ti_2O_7$

I-1 Energies of the different sites

First, we provide the energies (in eV) of the two defects in their different possible sites, relative to the most stable one (apical in n = 1, bridging apical in n=2).

n = 1 (Sr_2TiO_4) U = 3 eV J = 0 eV

H/vacancy position	Hydride	O vacancy
Apical	0.00 (GGA+U : 0.00)	0.00 (GGA+U : 0.00)
Equatorial	0.24 (GGA+U : 0.17)	0.12 (GGA+U : 0.20)

The n = 1 system with the hydrides in the two positions has been computed also with other values of (U, J), giving very similar results:

U = 3 eV (4 eV), J = 1 eV

H position	Hydride
Apical	0.00 (0.00)
Equatorial	0.28 (0.27)

n = 2 ($Sr_3Ti_2O_7$)

H/vacancy position	Hydride	O vacancy
Apical	0.17	0.32
Bridging apical	0.00	0.00
Equatorial	0.28	0.40

I-2 Electronic structure

We focus on the electronic structure of the most stable defective systems. While the perfect systems are found insulators (Fig. 8 of the main text), the hydrided and oxygen-deficient systems are found metallic, with states at the bottom of the conduction band occupied, consistently with

the fact that the two defects considered (hydrides, O vacancy) are single and double donors (Fig. 8). In the present calculations, the electron(s) released by the defects do not localize on a single Ti atom (under the form of a small polaron Ti^{3+}) but remain delocalized over several Ti atoms in the supercell, and the newly occupied state(s) mainly appear(s) as linear combination(s) of 3*d* Ti orbitals.

Several electronic states with very close total energies may be found. For instance, in the bridging apical site of the O vacancy, we find a slightly magnetic state (with very small magnetic moments ~ 0.04 μ_B on half of the Ti atoms, and < 0.001 on the others), or a non-magnetic state with a magnetic moment < 0.002 μ_B on all the Ti. These two electronic configurations have, however, total energies that only differ by less than 1 meV. The same degeneracy has been observed for the hydride ion at this same site between two states, the one with half the Ti having magnetic moments ~ 0.06 μ_B with the same sign (the other close to zero, i.e. < 0.0001 μ_B), the other with half the Ti having moment ~ 0.06 μ_B with alternating signs, so that the supercell has no net magnetic moment. Both have however energies identical within 1 meV. Thus, several electronic configurations are observed in some cases, but this degree of freedom does not change significantly the energy of the configuration.

I-3 Optimized lattice constants

n = 1

Model	*a* (Å)	*c* (Å)
Perfect systems	3.856	12.392
Defective systems: Hydride	3.864	12.376
Defective systems: O vacancy	3.867	12.385

n = 2

Model	*a* (Å)	*c* (Å)
Perfect systems	3.871	20.088
Defective systems: Hydride	3.875	20.063
Defective systems: O vacancy	3.878	20.060

(for comparison: pure $SrTiO_3$ computed with the same numerical scheme in a cubic $Pm\bar{3}m$ cell: LDA : $a = b = c = 3.863$ Å, LDA+U : $a = b = c = 3.879$ Å).

I-4 Atomic distortions

n = 1 : The hydride increases significantly its distance with respect to its neighboring Ti compared to the O atom in the perfect system:
perfect O-Ti along z : 1.979 Å
H-Ti (apical site): 2.162 Å

n = 2: in the bridging-apical configuration for both defects, the two neighboring Ti atoms are significantly pushed away by the defect, which can be quantified by the distance between these two Ti:
n = 2 (perfect): 3.935 Å
n = 2 H bridging-apical: 4.123 Å
n = 2 O vacancy bridging-apical: 4.327 Å

I-5 Charged supercells

In the n=2 compound, we have recomputed the H impurity in charge state +1, and the O vacancy in charge states +1 and +2. Here the lattice constants are fixed to those of the perfect system and not relaxed. We obtain the same order as for the neutral defects:

	Hydride q = +1	O vacancy q = +2	O vacancy q = +1
Apical	0.17	0.53	0.50
Bridging apical	0.00	0.00	0.00
Equatorial	0.32	0.74	0.62

II – Strontium vanadate Sr_2VO_4 with hydride impurities

II-1 Perfect system

As indicated in the main text, the present LDA+U calculations do not pretend to capture all the complexity of the electronic structure of this strongly-correlated electron compound. We expect, however, a correct description of charge localization and bonding. We have used U = 5 eV and J = 0 eV on the d states of vanadium, but tests have been performed using U = 3.5 eV and J = 0 eV, and using U = 5 eV and J = 0.7 eV.

In Sr_2VO_4, the V ions are in the +4 charge state (electronic structure $3d^1$). By contrast with the titanate compounds previously presented, Sr_2VO_4 is a Mott insulator: the occupied $3d$ states are stabilized by strong electronic correlations, and energetically located at the top of the valence

band, just above the 2*p* states of oxygen. The bandgap therefore separates the occupied *3d* states of V from the unoccupied *3d* states of this atom. The compound is assumed as antiferromagnetic, with the sign of the magnetic moments alternating along the *x* and *y* Cartesian directions.

II-2 Hydrides

One H atom is introduced in the 56-atom supercell, replacing either an apical or an equatorial oxygen (it corresponds to a system with chemical formula $Sr_2VO_{3.875}H_{0.125}$). After structural optimization, we observe that the electron released by the H^- defect is localized on a V atom next to the H (formally it is a V^{3+}). This is clearly visible on the atomic magnetic moments: the magnetic moment of the reduced V evolves from 0.9 to 1.7 μ_B, while all the other V atoms retain a magnetic moment of 0.9 μ_B. This behavior is the same whether $U = 3.5$ eV or $U = 5$ eV.

Second, in contrast to the titanate compounds, H^- is found as more stable in the equatorial site than on the apical one. The energies of the different configurations (relative to the most stable) are:

(U, J) (eV)	$U = 5$, $J = 0$	$U = 3.5$, $J = 0$	$U = 5$, $J = 0.7$
Apical	0.14	0.18	0.15
Equatorial	0.00	0.00	0.00