−Communication−

Thermodynamic Stability of SrCeO₃ in Aqueous Solutions at 298 K and in a High-temperature Reductive Atmosphere

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Strontium Cerate(SrCeO₃)-based perovskites have been extensively investigated as proton conductors by Iwahara and coworkers[1,2]; they also investigated on chemical stability in aqueous solutions at room temperature and at various high-temperature atmospheres. The objective of the present communication is to make thermodynamic analyses on its stability by using chemical potential diagrams for the Sr-Ce-O-H-e⁻ system at 298 K and for the Sr-Ce-O system at 1273 K; these diagrams are compared with experimental results by Uchida et al.[2]

High Temperature thermodynamic properties of SrCeO₃ have been determined by Levitskii et al.[3] from emf measurements as follows;
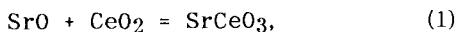
$$SrO + CeO_2 = SrCeO_3, \qquad (1)$$
$$\Delta_r G^\cdot = \Delta_r H^\cdot - T\Delta_r S^\cdot$$
$$= (-7200 - 8.9 \ T/K) \ J/mol. \qquad (2)$$

The enthalpy of formation at 298 K and other functions listed in Table 1 were derived from above equations together with estimated heat capacities. The chemical potential diagram for the Sr-Ce-O system was constructed at 1273 K using the computer program, CHD.[4,5] Figure 1 shows the log P(O₂) vs. log {a(Ce)/a(Sr)} plot, where P and a are the partial pressure and the activity, respectively; CeO₂₋ₓ was treated as a

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Key words: Strontium Cerate, Stability, Decomposition, Dissolution

nonstoichiometric compound[6,7] using the SOLGASMIX program.[8,9] Figure 1 indicates that SrCeO₃ may decompose at an extremely reductive atmosphere as follows[10];

$$SrCeO_3 = SrO + 1/2Ce_2O_3 + 1/4O_2(g). \qquad (3)$$
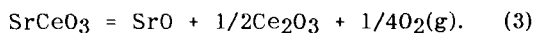
The equilibrium oxygen partial pressure over a mixture of SrCeO₃, SrO and Ce₂O₃ is given as 1.62×10^{-22} atm; this corresponds to log P(H₂O)/P(H₂) = -3.6. This confirms that SrCeO₃ is in a practical sense stable even in pure hydrogen. Actually, Iwahara et al.[11] observed from X-ray diffraction studies that Yb-doped SrCeO₃ (SrCe₀.₉₅Yb₀.₀₅O₃₋δ) was stable in wet hydrogen gas (P(H₂O) = 0.013-0.026 atm) at 1273 K whereas in dry hydrogen gas (dew point < 233 K), it was partially reduced to form Ce₂O₃.

The electrochemical potential diagram for the Sr-Ce-O-H-e⁻ system was constructed as follows: We have recently constructed the electrochemical potential diagrams for multicomponent systems[12] and applied to gain insight of the stability of double oxides in aqueous solutions.[13] From these chemical thermodynamic considerations, the following criteria were derived to examine the stability of double oxides in aqueous solutions:

(1) Hydration reaction cannot proceed unless the dissolved species promotes reconstruction of cations which is needed for precipitation of other solid state compounds.

(2) Thus, the equilibrium between the double oxide to be considered and aqueous species becomes quite important

Table 1. Thermodynamic functions of compounds (sl,c) and aqueous species (ao) at 298 K in the Sr-Ce-O-H-e$^-$ system: Enthalpy of formation, $\Delta_f H°$, Gibbs energy of formation, $\Delta_f G°$, and standard entropy, $S°$, at 298 K and coefficients of high temperature heat capacity equation: $C_p = a + 10^{-3} b (T/K) + 10^5 c (K/T)^2$.

substance	state	$\Delta_f H°$ kJ/mol	$\Delta_f G°$ kJ/mol	$S°$ J/mol K	a	b	c	ref.
						J/mol K		
$Ce_{0.8}O_{1.2}$	sl[1]	-672.2	-642.6	81.20	43.13	16.56	-3.68	6,7
CeO_2	sl	-1088.7	-1024.6	62.30	64.81	17.70	-7.594	6,7
SrO	c	-592.0	-561.9	54.4	49.82	6.75	-5.86	9
$SrCeO_3$	c	-1687.9	-1596.6	125.6	114.63	24.45	-13.45	3
Ce^{3+}	ao	-696.2	-672.	-205.				14
Sr^{2+}	ao	-545.80	-559.48	-32.6				14
$SrOH^+$	ao		-721.3					14

[1] The interaction parameter of the subregular solution (sl) between CeO_2 and $Ce_{0.8}O_2$ is given as $\omega/kJ\ mol^{-1} = [-70.21 + 63.765\ (x1-x2)] - [-32.05 + 32.05\ (x1-x2)](T/K)$, where x1 and x2 are mole fraction of CeO_2 and $Ce_{0.8}O_2$, respectively.

to see whether or not the double oxide can dissolve into solutions.

(3) When double oxides dissolve into aqueous solutions, dissolved metallic ions remain as aqueous species or precipitate as hydrated compounds. In the latter case, the system may move to other equilibria containing the precipitated phase or may not reach equilibrium until the initial double oxide completely disappears; in this sense, the presence of water promotes the reconstructive reaction.
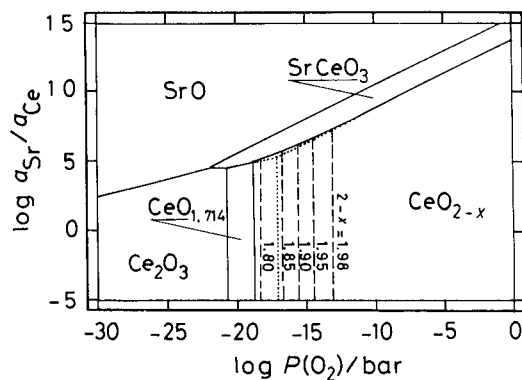
In the present communication, the stability of $SrCeO_3$ is examined according to the above considerations: First, the hydration reaction of $SrCeO_3$ can be written as
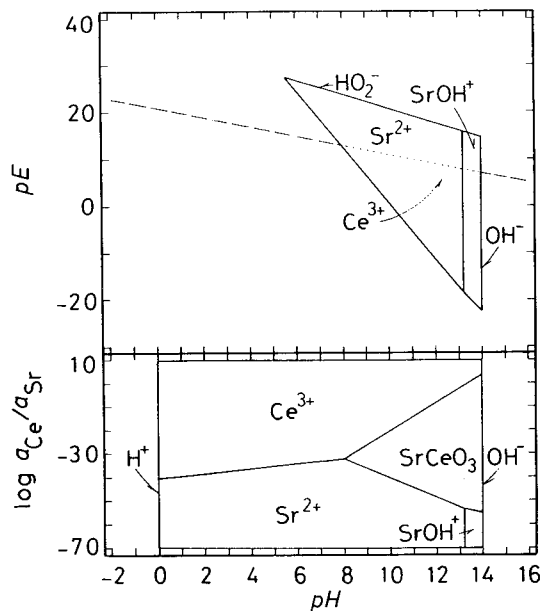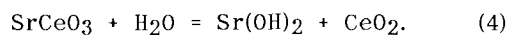

Fig. 2 Electrochemical potential diagram for Sr-Ce-O-H-e$^-$ (a(H$_2$O)=1) system at 298 K. The upper shows the stability region of SrCeO$_3$ presented in a pE vs. pH plot, whereas the lower shows the equilibria between SrCeO$_3$ and aqueous species at P(O$_2$) = 1 bar.

Fig. 1 Chemical potential diagram for Sr-Ce-O system at 1273 K. Selected oxygen stoichiometric numbers of CeO$_{2-x}$ are given.

$$SrCeO_3 + H_2O = Sr(OH)_2 + CeO_2. \quad (4)$$

The Gibbs energy change for this reaction can be calculated as -63.1 kJ/mol, indicating that $SrCeO_3$ is metastable in the presence of water. As a next step, the electrochemical potential diagram has been constructed to examine the solid-liquid equilibria between $SrCeO_3$ and aqueous species. Fig. 2 shows that $SrCeO_3$ is in equilibrium with Sr^{2+} and Ce^{3+} at $P(O_2)$=1 bar, and this combination corresponds to the following dissolving reaction;

$$SrCeO_3 + 3\ H_2O + e^-$$
$$= Sr^{2+} + Ce^{3+} + 6\ OH^-. \quad (5)$$
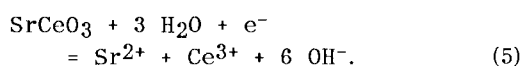
Uchida et al.[2] experimentally found that $SrCeO_3$ dissolved into hydrochloric acid to evolve $Cl_2(g)$. This reaction can be written as

$$SrCeO_3 + 3\ H_2O + Cl^-$$
$$= Sr^{2+} + Ce^{3+} + 6OH^- + 1/2Cl_2(g). \quad (6)$$
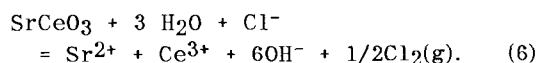
This is completely consistent with the present calculational results given by eq. (5). Uchida et al. also found that $SrCeO_3$ slightly dissolved in water, and as a result, the solution became slightly alkaline. In the vicinity of pH = 7, Ce^{3+} tends to precipitate as follows;

$$Ce^{3+} + 4\ OH^- = CeO_2 + 2\ H_2O + e^-. \quad (7)$$
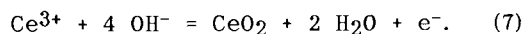
Since strontium remains as the aqueous species, the overall reaction after combining eqs. (5) and (7) is given as

$$SrCeO_3 + H_2O = Sr^{2+} + CeO_2 + OH^-. \quad (8)$$
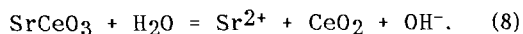
This confirms that a slight dissolution of $SrCeO_3$ into water should be accompanied with the increase of pH; note that with increasing pH, $SrCeO_3$ becomes stable against dissolution and finally approaches the equilibrium state with aqueous species.

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