Supporting Information

Structure and electronic properties of $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} \cdot 4\text{e}^-$ surfaces: opportunity for controlled charge transfer

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Here we compare surface energies obtained from local density approximations (LDA) and Perdew-Burke-Ernzerhoff (PBE) functional form of the generalized gradient approximation (GGA). We show results on variation of oxygen chemical potential, $\Delta \mu_O$, as a function of temperature and oxygen pressure. Finally, we show variation of nominal ionic charge of a lattice cage along a surface normal.

Figure S1 shows free energy as a function of $\Delta \mu_O$ (bottom axis) and $\Delta \mu_{Ca}$ (top axis), obtained from LDA and PBE approximations for (001)$_1$, average of (111)$_1 X^+_3$ and $X^{-3}$, and (110)$_1 X_{t}$, $X_{s}$, and $Z_{s}$ surface. It shows that the PBE surface energies are lower by 25 − 35%, compared to those obtained by the LDA. Moreover, crossover points where reversal of relative stability occurs are significantly shifted. Consequently, these altogether can reverse
Figure S1: Left panel: free energy as a function of $\Delta \mu_O$ (bottom axis) and $\Delta \mu_{Ca}$ (top axis), obtained from LDA and PBE approximations for (001)$X$ and average of (111)$X^3_+$ and $X^3_-$ surface. The shaded area indicate the $\Delta \mu_O$ interval corresponding to temperature $\sim$900-1050$^\circ$C and pressure $\sim$10$^{-8}$ used for surface preparation. Right panel: the same as the left one but for (110)$X_l$, $X_s$, and $Z_s$ surface.

relative stability of the surfaces. For example, PBE free energy of the (110)$Z_s$ is lower than that of the (110)$X_l$ around $\Delta \mu_O = -3.0$ eV; but the opposite is predicted by the LDA results. Nevertheless, the LDA and PBE results are consistent on relative stability of the surfaces at O-rich/Ca-poor and O-poor/Ca-rich conditions. In addition, the surface energies are close to one another under the experimental conditions of temperature $\sim$900 – 1050$^\circ$C and pressure $\sim$10$^{-8}$ (shaded areas) used for surface preparation.$^1$

Figure S2 shows dependence of variation of oxygen chemical potential, $\Delta \mu_O$, on temperature and oxygen pressure. The variation $\Delta \mu_O$ is defined by referring chemical potential of oxygen species, $\mu_O$, to one half of the energy of the O$_2$ in its triplet ground state: $\Delta \mu_O = \mu_O - E(O_2)/2$. The dependence of $\mu_O$ on temperature, $T$, and oxygen pressure, $p_{O_2}$, is governed by the Maxwell's relation $(\partial \mu_O/\partial p_{O_2})_T = (k_B T/2)/p_{O_2}$, where $k_B=8.617 \times 10^{-5}$ eV/K is the Boltzmann constant. Details on solution of this equation have
been published elsewhere.\textsuperscript{2,3} Under the experimental conditions, $\Delta \mu_O$ varies from $-3.3$ to $-2.8$ eV (closed dashed line).

Figure S3 shows variation of nominal ionic charge, $Q_{cage}$, of a lattice cage along a surface normal for the (001)$X||X$, (110)$X_\ell$ and $Z_{sv}$, and (111)$X^3_3||X^3_3$ slab. The $Q_{cage}$ of a cage $k$ is calculated by $Q_{cage}(k) = \sum_{i=1}^{N} Z_{i,k}/n_{i,k}$, where $N = 30$ is the number of atoms per cage; $Z_{i,k}$ and $n_{i,k}$ are nominal ionic charge and order of atom $i$ in the cage $k$, respectively. The $n_{i,k}$ is the number of cages which share the atom $(i, k)$. In the bulk-like region, $Q_{cage}$ attains the value of $|e|/3$, which is the ionic charge of a lattice cage in a bulk C12A7:$e^-$. For all of the slabs, $Q_{cage}$ is considerably increased at the terminating cage layers. This causes extra-framework electrons to accumulate at the surfaces. Interestingly, the subsurface layers has negative $Q_{cage}$ values, meaning an electronic charge depletion in these layers. For the (001) and (110) slabs, $Q_{cage}$ behavior is symmetric, indicating equivalent charge distributions at the top and bottom surfaces. In contrast, for the (111)$X^3_-||X^3_+$ slab, $Q_{cage}$ shows an asymmetric behavior with a much higher ionic charge at the top surface $X^3_+$. Consequently, electronic
Figure S3: Variation of nominal ionic charge $Q_{\text{cage}}$ of a lattice cage along a surface normal for the (001) $X||X$, (110) $X_{\ell}$ and $Z_{s}$, and (111) $X_{3}^{\perp}||X_{3}^{\perp}$ slab. For each case, two different slab thicknesses, $w$ (number of cage layers), are considered. The horizontal dashed lines indicate $Q_{\text{cage}}$ value of a cage in a bulk C12A7:$e^{-}$.

charge density is considerably higher at the top surface, compared to the bottom one, $X_{3}^{\perp}$.

References

(1) Yoshitake Toda and Yousuke Kubota and Masahiro Hirano and Hiroyuki Hirayama and Hideo Hosono, ACS Nano 5, 1907-1914 (2011)
