# Supporting Information of "Understanding Oxygen Non-Stoichiometry in Mayenite: from Electride to Oxygen Radical Clathrate"

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## S1. Chemical potential of oxygen molecule

The chemical potential of oxygen molecule is derived from experimental data in this study. The heat capacity and the entropy have been determined experimentally under standard conditions (298.15 K, 1 bar) and as functions of temparture.<sup>1,2</sup> The Gibbs free energy at given (T, P) can be related with the experimental data by,

$$G(T,P) = G(T,P) - G(T^{\text{std}},P^{\text{std}}) + G(T^{\text{std}},P^{\text{std}}) - G^0 + G^0$$
(s1)

where  $G^0$  is the free energy at zero temperature. The free energy at zero temperature only has an internal energy term  $U^0$  which includes the O<sub>2</sub> potential energy calculated by DFT and a zero-point energy known from experiments. As such, the last three terms in Equation s1 can be determined by,

$$G^{\text{std}} - G^0 + G^0 = H^{\text{std}} - S^{\text{std}}T^{\text{std}} - H^0 + U^0 = \left[H^{\text{std}} - H^0\right] - S(T^{\text{std}})T^{\text{std}} + U^0$$
(s2)

In the above equation,  $H^{\text{std}} - H^0$  is taken from the experimental value of 8.680 eV, and  $U^0 = E^{\text{DFT}} + E^{\text{ZP}}$ , where the experimental value of  $E^{\text{ZP}}$  is 0.0976 eV and the  $E^{\text{DFT}}$  is calculated from DFT simulations as detailed in the main text.

From here, we introduce an intermediate state  $(T, P^{\text{std}})$  to calculate  $G(T, P) - G(T^{\text{std}}, P^{\text{std}})$  by:

$$G(T,P) - G(T^{\text{std}},P^{\text{std}}) = G(T,P) - G(T,P^{\text{std}}) + G(T,P^{\text{std}}) - G(T^{\text{std}},P^{\text{std}})$$
(s3)

where G(T, P) is calculated following the ideal gas law:

$$G(T,P) - G(T,P^{\text{std}}) = RTln(P/P^{\text{std}})$$
(s4)

Thus,

$$G(T,P) - G(T^{\text{std}},P^{\text{std}}) = RTln(P/P^{\text{std}}) + H(T,P^{\text{std}}) - H(T^{\text{std}},P^{\text{std}}) - S(T)T + S(T^{\text{std}})T^{\text{std}}$$
(s5)

And we have

$$H(T, P^{\text{std}}) - H(T^{\text{std}}, P^{\text{std}}) = \int_{T_{\text{std}}}^{T} C_{P^{\text{std}}} dT$$
(s6)

Altogether, the free energy for oxygen gas can be expressed as

$$G_{\text{gas}}(T,P) = U^0 + \left[H^{\text{std}} - H^0\right] + RT\ln\left(\frac{p}{p^{\text{std}}}\right) + \int_{T_{\text{std}}}^T C_{p^{\text{std}}}(T)dT - S(T,P^{\text{std}})T$$
(s7)

where the heat capacity,  $C_{p^{\text{std}}}(T)$ , and entropy,  $S(T, P^{\text{std}})$ , for oxygen gas can be obtained from literature<sup>3</sup>. After converting the Gibbs free energy to chemical potential for different (T, P), we can then use Equation 9 in the main text to calculate the equilibrium conditions for redox reactions involving oxygen molecules.

### **S2.** Structures

The simulated lattice parameters as a function of oxygen non-stoichiometry  $\delta$  (detailed in the main text) are shown in Figure S1. Overall, the lattice parameter varies only slightly during redox. At stoichiometry ( $\delta$ =1), the simulation result agrees well with the experimental data.<sup>4,5</sup> For mayenite with  $\delta$ <2 in both O and O<sub>2</sub> -clathrate forms, the lattice parameters increase roughly linearly with the reduction level. On the other hand, oxidized O and O<sub>2</sub> -clathrate mayenites ( $\delta$ >2) show different trends in lattice parameter versus the degree of non-stoichiometry. The lattice parameter of the O<sub>2</sub>-clathrate mayenite increases as a function of  $\delta$ , whereas that of the O-clathrate mayenite remains roughly constant. This slight change of the mayenite lattice with oxygen non-stoichiometry would reveal when the experimental samples were synthesized through different processes.<sup>6</sup>



Figure S1. Lattice parameters of O and O<sub>2</sub> -clathrate mayenite as a function of oxygen non-stoichiometry  $\delta$ . Simulated lattice parameter of stoichiometric O-clathrate mayenite agrees with the experimental data (~0.17% difference).<sup>4,5</sup>

#### S3. Electronic partial density of states

From the partial electronic density of states (eDOS) in Figure S2, it can be seen that the gap states of non-reduced mayenite, i.e., those between 1-2 eV for O-clathrate and around 1 eV for O<sub>2</sub>-clathrate, are associated with the clathrated oxygen species, as discussed in the main text. The bottom states of the conduction bands with a density peak at respectively around 5 or 4.5 eV for O or O<sub>2</sub> -clathrate mayenite, are usually referred to as "cage conduction bands".<sup>7,8</sup> The O<sub>2</sub>-clathrate also has extra states in the conduction band located at 5.2 eV corresponding to higher O-O molecular orbitals.



Figure S2. Partial electronic density of states (eDOS) of O (a) and  $O_2$  (b) -clathrate mayenite, projected on Al, Ca, network O and clathrated O/O<sub>2</sub>, respectively. The gap states (green peaks around 1 eV) are contributed by the clathrated O/O<sub>2</sub>.

#### **S4.** Phonon properties

The phonon properties are calculated using the TDEP method, as detailed in the main text. Figure S3 shows that C12A7:  $2e^-$ , C12A7:  $10^{2-}$  and C12A7:  $10_2^{2-}$  have a similar phonon DOS in general, which is expected because they share the same Ca-Al-O framework structure. The presence of loosely-bound clathrated species in the case of O and O<sub>2</sub> -clathrate mayenite give rise to softening of the phonon modes at low frequencies (smaller than 100 cm<sup>-1</sup>). The motions of clathrated O or O<sub>2</sub> also lead to smoothing of the phonon DOS at higher frequencies and bring extra phonon states within 600-750 cm<sup>-1</sup>.

These differences in the phonon DOS of different clathrates, however, only translate to minor changes in their thermodynamic properties, such as heat capacity and entropy, as shown in Figure S4. The calculated heat capacities for different clathrates all agree well with those from previous experiments and simulations.<sup>9,10</sup> Therefore, the redox free energy (seen Equation 5 and 9 in the main text) is mainly controlled by the enthalpic contribution, i.e., the redox energy calculated from DFT relaxations.



Figure S3. Phonon density of states (DOS) of C12A7:  $2e^-$ , C12A7:  $10^{2-}$ , and C12A7:  $10_2^{2-}$ .



Figure S4. Heat capacity and entropy of C12A7:  $2e^-$ , C12A7:  $10^{2^-}$ , and C12A7:  $10^{2^-}$  up to 1750 K. The calculated heat capacities are in agreement with experimental data and previous simulation results.<sup>9,10</sup> Both heat capacity and entropy vary slightly depending on the clathrated species, e.g., O vs. O<sub>2</sub>.

#### Reference

- (1) Irikura, K. K. Experimental Vibrational Zero-Point Energies: Diatomic Molecules. *Journal of Physical and Chemical Reference Data* **2007**, *36* (2), 389–397. https://doi.org/10.1063/1.2436891.
- (2) Haynes, W. M. CRC Handbook of Chemistry and Physics; CRC press, 2014.
- (3) Chase, M. W. NIST-JANAF Themochemical Tables, Fourth Edition. J. Phys. Chem. Ref. Data, Monograph 9 1998, 1–1951.
- Palacios, L.; De La Torre, Á. G.; Bruque, S.; García-Muñoz, J. L.; García-Granda, S.; Sheptyakov, D.; Aranda, M. A. G. Crystal Structures and In-Situ Formation Study of Mayenite Electrides. *Inorg. Chem.* 2007, *46* (10), 4167–4176. https://doi.org/10.1021/ic0700497.
- (5) Sakakura, T.; Tanaka, K.; Takenaka, Y.; Matsuishi, S.; Hosono, H.; Kishimoto, S. Determination of the Local Structure of a Cage with an Oxygen Ion in Ca12Al14O33. *Acta Cryst B* 2011, 67 (3), 193–204. https://doi.org/10.1107/S0108768111005179.
- (6) Rashad, M. M.; Mostafa, A. G.; Rayan, D. A. Structural and Optical Properties of Nanocrystalline Mayenite Ca12Al14O33 Powders Synthesized Using a Novel Route. *J Mater Sci: Mater Electron* 2016, 27 (3), 2614– 2623. https://doi.org/10.1007/s10854-015-4067-z.
- Kim, S. W.; Matsuishi, S.; Nomura, T.; Kubota, Y.; Takata, M.; Hayashi, K.; Kamiya, T.; Hirano, M.; Hosono, H. Metallic State in a Lime–Alumina Compound with Nanoporous Structure. *Nano Lett.* 2007, 7 (5), 1138–1143. https://doi.org/10.1021/nl062717b.
- (8) Sushko, P. V.; Shluger, A. L.; Hirano, M.; Hosono, H. From Insulator to Electride: A Theoretical Model of Nanoporous Oxide 12CaO·7Al2O3. J. Am. Chem. Soc. 2007, 129 (4), 942–951. https://doi.org/10.1021/ja066177w.
- (9) Bonnickson, K. High Temperature Heat Contents of Aluminates of Calcium and Magnesium. The Journal of

*Physical Chemistry* **1955**, *59* (3), 220–221.

 (10) Huang, J.; Valenzano, L.; Sant, G. Framework and Channel Modifications in Mayenite (12CaO·7Al2O3) Nanocages By Cationic Doping. *Chem. Mater.* 2015, 27 (13), 4731–4741. https://doi.org/10.1021/acs.chemmater.5b01360.