Supplementary Information
Oxygen exchange kinetics of $BaGd_{0.3}La_{0.7}Co_2O_{6-\delta}$ with exsolved Co_3O_4 nanoparticles in dry and humid atmospheres

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1 Synchrotron X-ray diffraction

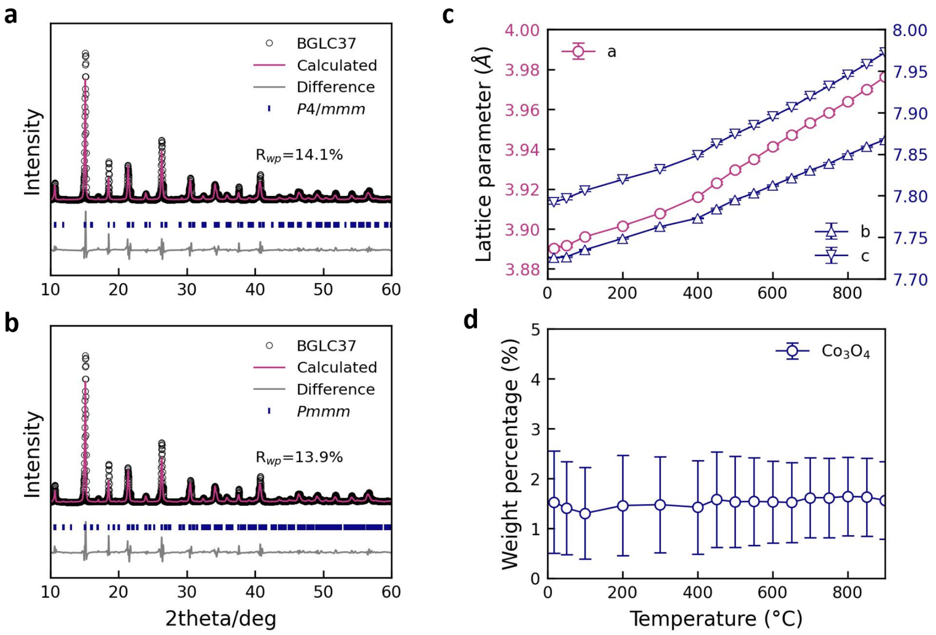

Figure 1: Rietveld refinements of synchrotron X-ray diffraction data of $BaGd_{0.3}La_{0.7}Co_2O_{6-\delta}$ using (a) tetragonal P4/mmm and (b) orthorhombic (*Pmmm*) structures, showing the observed experimental (black circles), calculated (red line), difference (green line) and hkl ticks of fitting phases (c) Temperature-dependent lattice parameters of primary *Pmmm* phase. (d) Co_3O_4 weight percent obtained from Rietveld refinements using a two-phase model comprising of *Pmmm* and minor Co_3O_4 content of ~1 wt%.

2 Pulsed isotope exchange

2.1 Dry carrier gas

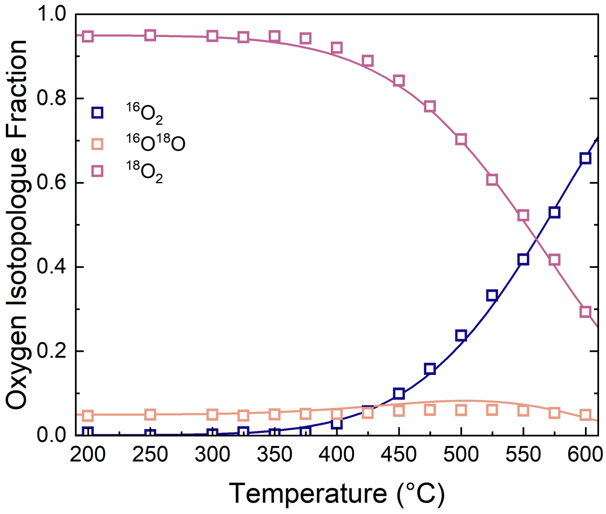

Figure 2: Oxygen isotopologue fractions as a function of temperature at 0.02 bar O_2. The solid lines are fitted according to the two-step adsorption/incorporation model.

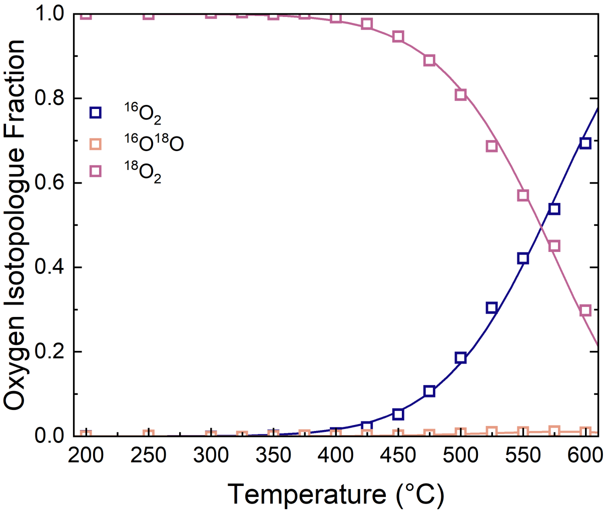

Figure 3: Oxygen isotopologue fractions as a function of temperature at 0.005 bar O_2. The solid lines are fitted according to the two-step adsorption/incorporation model.

2.2 Humid carrier gas

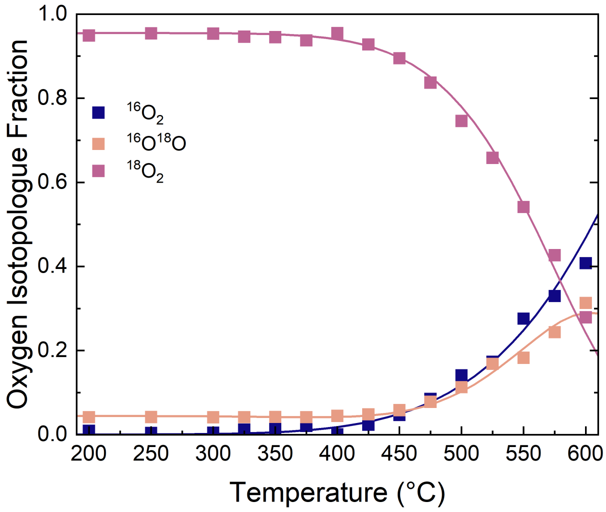

Figure 4: Oxygen isotopologue fractions as a function of temperature at 0.21 bar O_2. The solid lines are fitted according to the two-step adsorption/incorporation model.

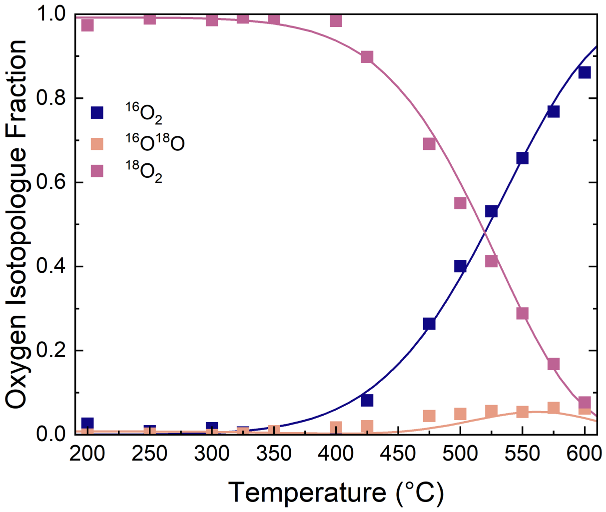

Figure 5: Oxygen isotopologue fractions as a function of temperature at 0.02 bar O_2. The solid lines are fitted according to the two-step adsorption/incorporation model.

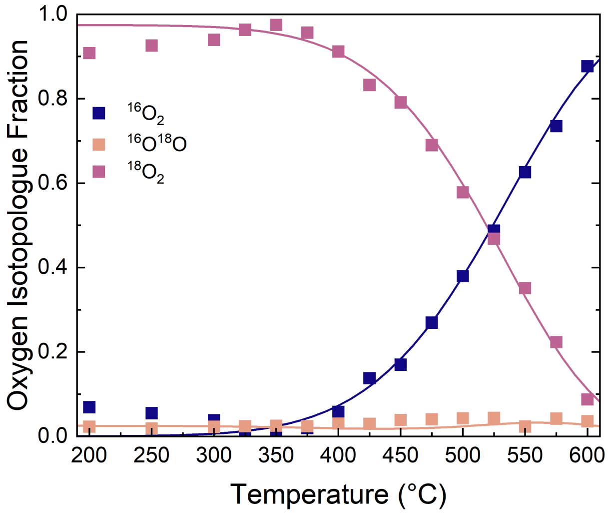

Figure 6: Oxygen isotopologue fractions as a function of temperature at 0.005 bar O_2. The solid lines are fitted according to the two-step adsorption/incorporation model.

2.3 Oxygen exchange with water

When water is introduced into the carrier gas, additional reactions may occur that can impact the overall exchange rate:

$$^{18}O_2 + 2H_2{}^{16}O \rightarrow {}^{16}O_2 + 2H_2{}^{18}O \quad \text{Eq. 1}$$

$$^{18}O_2 + H_2{}^{16}O \rightarrow {}^{16}O^{18}O + H_2{}^{18}O \quad \text{Eq. 2}$$

$$^{18}O_{bulk} + H_2{}^{16}O \rightarrow {}^{16}O_{bulk} + H_2{}^{18}O \quad \text{Eq. 3}$$

The first two reactions may accour at the front and at at the tail of the pulse, *i.e.*, at the interface between the carrier gas and the pulse. These reactions are likely to be relatively negligible due to the length of the pulse. However, the third reaction, heteroexchange of water with the bulk, is more likely to occur.[1]

To determine whether oxygen from water contributes to the measured oxygen exchange, the evolutino of masses 17 (^{16}OH), 18 ($H_2{}^{16}O$), 19 (^{18}OH), and 20 ($H_2{}^{18}O$) was investigated. The raw data from the mass spectrometer (MS) is ion current which increases as the amount of a specific mass increases (increase in the area under the peak). An increase in the area under mass 20 was observed under the pulse, however, mass 20 comprises both Ar and $H_2{}^{18}O$. Therefore, to further look into the exchange of oxygen from water and oxygen gas/bulk oxygen, the ion currents of masses 17 (^{16}OH) and 19 (^{18}OH) were investigated. Mass 19 shows no remarkable increase with the pulse in dry while a peak is observed when wet carrier gas is utilised. The small peak in the ion current for mass 17 in dry atmosphere could be due to traces of water in the carrier gas, since the gas is nominally bottle dry and therefore may contain traces of water, or in the setup. In humid atmosphere the ion current from mass 17 decreases when the pulse is sent over the sample due to the dry pulse. The amount of mass 19 compared to the total amount of masses 19 and 20 (Table 1) shows that there is very limited exchange of oxygen from the gas with oxygen from water molecules in the carrier gas. Therefore, exchange with water was considered not to have any significant effect on the oxygen exchange rate. For a substantial amount of oxygen exchange to be observed, the amount of mass 19 compared to the total amount of masses 19 and 20 is expected to be roughly 0.21. As the pO_2 is decreased, even less exchange with the water molecules is observed.

Table 1: Amount of mass 19 compared to the amount of mass 19 and mass 20 in wet carrier gas, calculated from the area under the ion current peaks.

pO_2 (bar)	**m19/(m19+m20)**
0.21	0.14 – 0.04
0.02	0.09 – 0.0
0.005	0.07 – 0.0

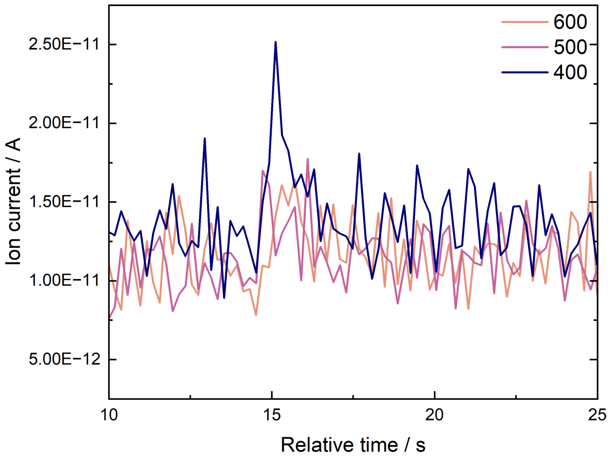

Figure 7: Ion current of mass 19 in dry carrier gas at 400, 500, and 600°C

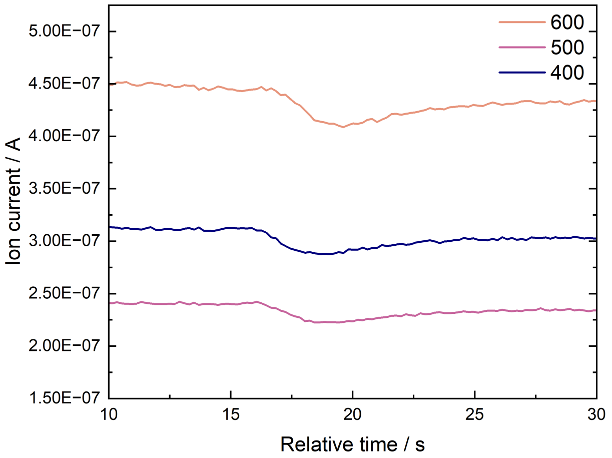

Figure 8: Ion current of mass 17 in dry carrier gas at 400, 500, and 600°C

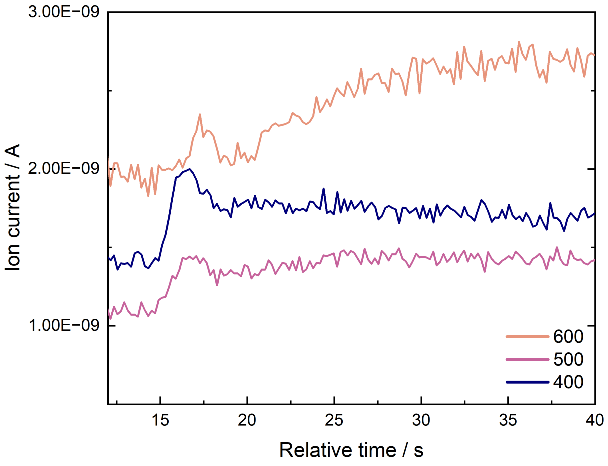

Figure 9: Ion current of mass 19 in humid carrier gas at 400, 500, and 600°C

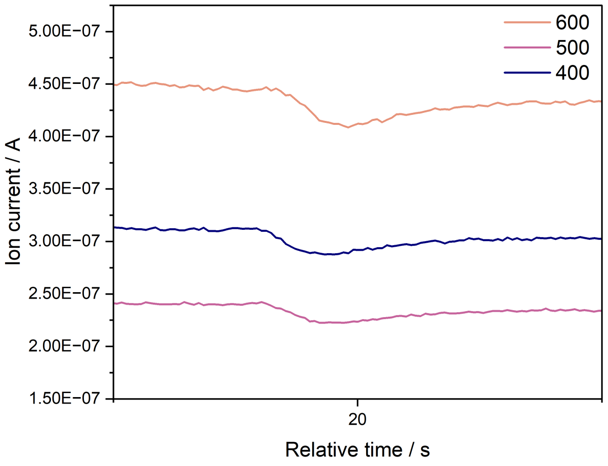

Figure 10: Ion current of mass 17 in humid carrier gas at 400, 500, and 600°C

2.4 Oxygen exchange with reaction chamber

No oxygen exchange was observed in the empty reaction chamber until at 800°C and higher (Figure 11). The observed oxygen exchange originates from adsorbed oxygen atoms on the reaction chamber and not with lattice oxygen, as there is no decrease observed in the amount of ^{18}O at all measured temperatures. As the temperature region of interest is 400-600°C, no correction is needed for the exchange rates calculated for BGLC37 due to interactions of oxygen with the reaction chamber.

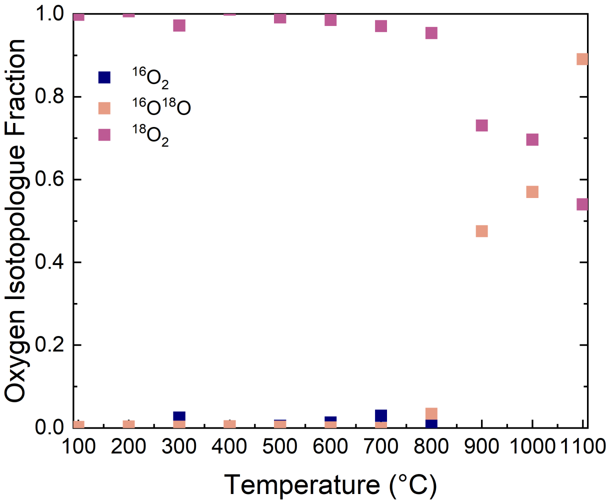

Figure 11: Background measurement of oxygen exchange in humid 0.02 bar O_2, empty reaction chamber.

3. References

1. V. Thoreton, M. Niania and J. Kilner, *Phys Chem Chem Phys*, 2021, **23**, 2805-2811.