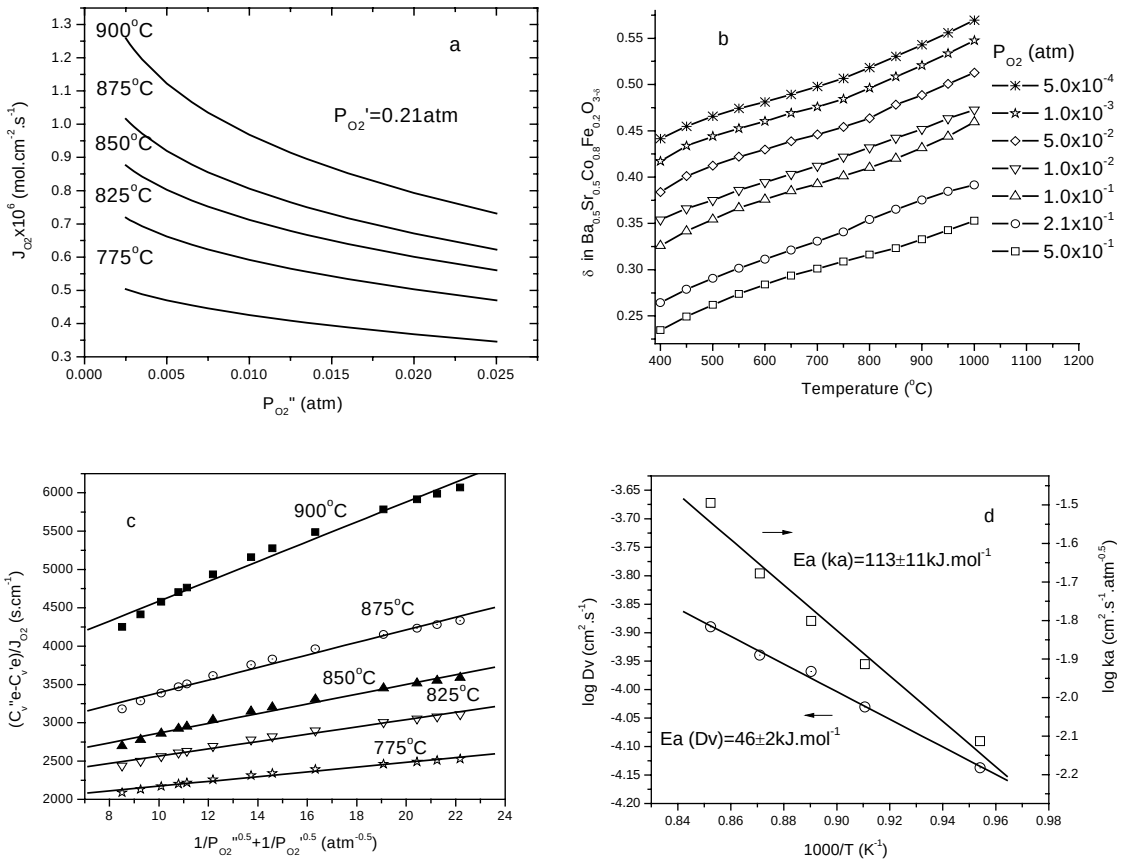

Supplementary Figure. 8. (a) Oxygen flux through BSCF as a function of oxygen partial pressure at the temperatures indication, (b) oxygen non-stoichiometry, δ, of BSCF as a function of temperature at the oxygen partial pressures indicated, (c) oxygen flux replotted for data analysis as described below, and (d) oxygen vacancy diffusion and surface exchange as functions of temperature, as derived from the data in parts (a) - (c). (See S7 for details of experimental procedure). Oxygen non-stoichiometry was obtained from thermal gravimetric analysis. The oxygen flux across a mixed oxide ion and electron conductor, in which electronic conductivity dominates the total conductivity and in which the Nernst-Einstein relationship accurately describes the relationship between ionic conductivity and ion diffusivity is given by

$$J_{O_2} = \frac{D_V}{2L}\left(C_V^{'',s} - C_V^{',s}\right)$$

where D_V is the oxygen diffusion coefficient, L is the thickness of the membrane and C_V^s is the oxygen vacancy concentration at the surface, with '' indicating the oxygen lean side and ' indicating the oxygen poor side [1]. For materials in which both surface exchange kinetics and bulk ion diffusion contribute to limiting the overall mass flux process, the surface vacancy concentration is not known *a priori*. It can be shown, however, under the reasonable assumption

that the concentration of electronic species is constant across the membrane (*i.e.* no voltage is generated), that the flux under the conditions of mixed control is given by

$$J_{O_2} = \frac{D_V}{2L}\left[\frac{1}{1+\frac{D_V}{2Lk_a}\left(P_{O_2}^{',-0.5}+P_{O_2}^{'',-0.5}\right)}\right]\left(C_V^{'',e}-C_V^{',e}\right)$$

where k_a is the surface exchange coefficient, PO_2 is the oxygen partial pressure, C_V^s is the oxygen vacancy concentration at the surface *under equilibrium conditions*, and '' and ' again indicate the oxygen rich and poor sides of the membrane [2]. This second equation can be rewritten as

$$\frac{\left(C_V^{'',e}-C_V^{',e}\right)}{J_{O_2}} = \frac{2L}{D_V}+\frac{1}{k_a}\left(P_{O_2}^{',-0.5}+P_{O_2}^{'',-0.5}\right)$$

and thus, a plot of $(C_v^{"e}-C_v^{'e})/J_{O2}$ verus $1/P_{O2}^{"0.5} + 1/P_{O2}^{'0.5}$, as presented in part (c), yields $2L/D_V$ as the intercept and $1/k_a$ as the slope. The linear nature of those curves, as well as the highly Arrhenius behavior of the derived D_V and k_a, part (d), demonstrate the validity of the approach developed. At 900 ^oC the oxygen diffusion coefficient of BSCF is 1.3×10^{-4} $cm^2.s^{-1}$ and the surface exchange coefficient is 3×10^{-2} $cm^2.s^{-1}.atm^{-0.5}$. The activation energies for these processes are 46 ± 2 $kJ.mol^{-1}$ and 113 ± 11 $kJ.mol^{-1}$, respectively.

[1] Bouwmeester,H.J.M. & Burggraaf, A.J. Dense ceramic membranes for oxygen separation. in: Gellings P.J. & Bouwmeester, H.J.M. (Eds.), The CRC Handbook of Solid State Electrochemistry, CRC Press, Boca Raton, pp. 481-553 (1997).

[2] Shao, Z.P. *et al.*, manuscript under preparation.