JAAS

PAPER

Electronic Supplementary Information

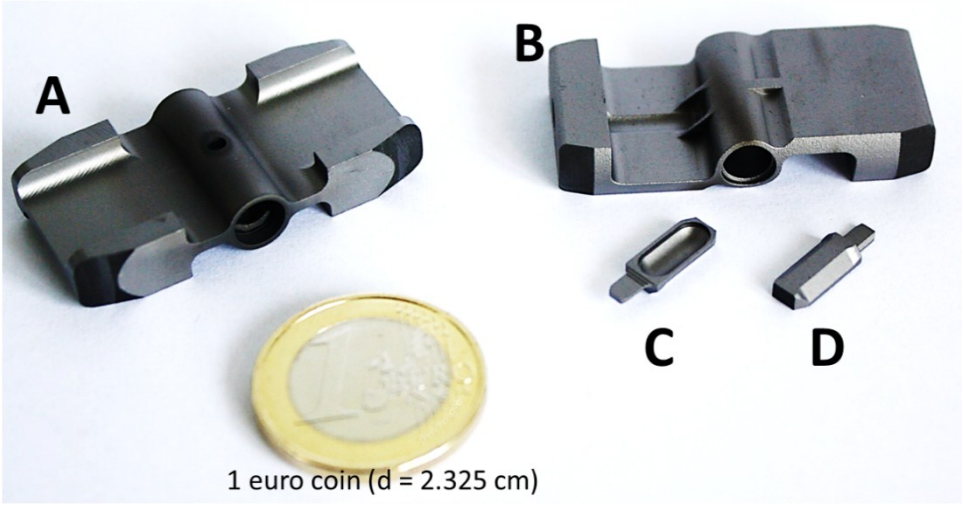

Fig. ESI 1. (A) Graphite tube with the incorporated platform used in HR-CS-AAS. (B) Graphite tube without platform used in solid sampling AAS. (C) Graphite platform for solid sampling, this platform is inserted in (B) with the sample. (D) backside of graphite platform for solid sampling (area 0.2 mm x 1 mm).

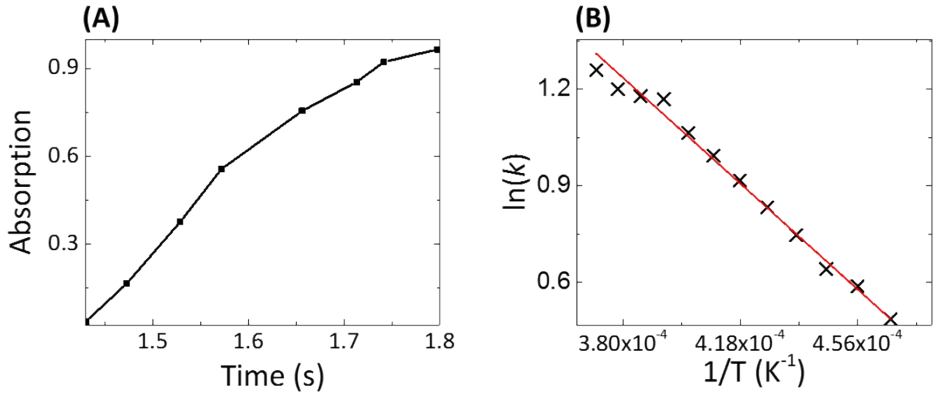

Fig. ESI 2. Determination of the order of reaction by analysing the slopes using the parameters from Arrhenius equation (Ea, k, T, t). (A) Abs. vs time. data for CaF formation at 2,400 °C and (B) Arrhenius plot ln(*k*) vs 1/T for CaF in a range of temperatures from 1,900 °C to 2,400 °C.

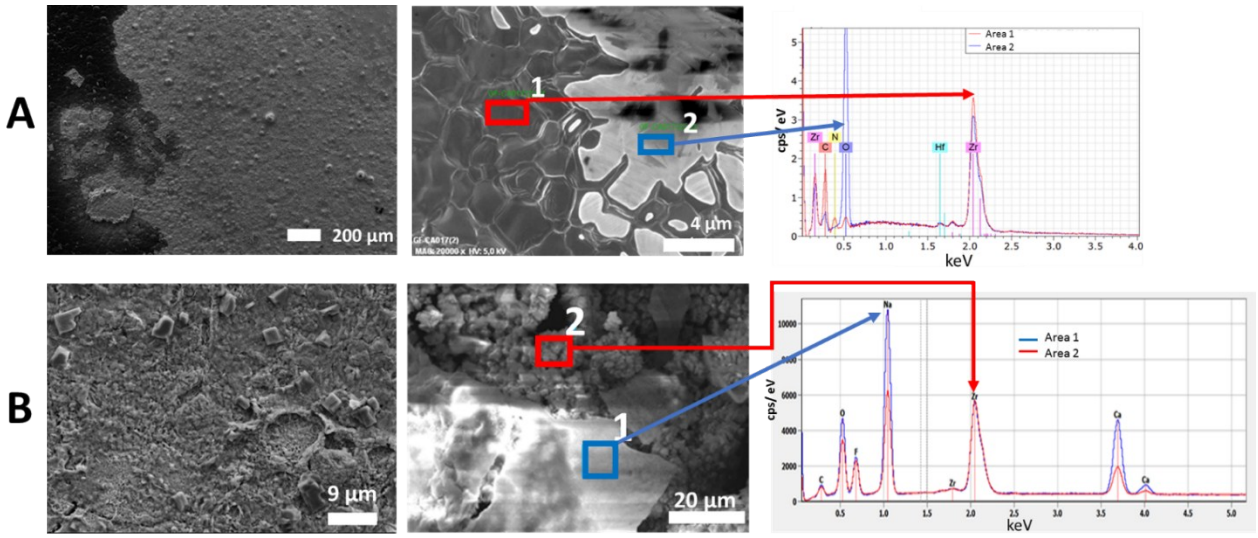

Fig. ESI 3. (A) SEM micrographs of a zirconium-coated graphite furnace P1 (overview and at higher magnification) and their corresponding EDX spectra at 5 kV for two apparently different areas. (B) SEM micrographs of the transition state P2 (overview and zoom and higher magnification) with their corresponding EDX spectra at 20 kV for two apparently different areas.

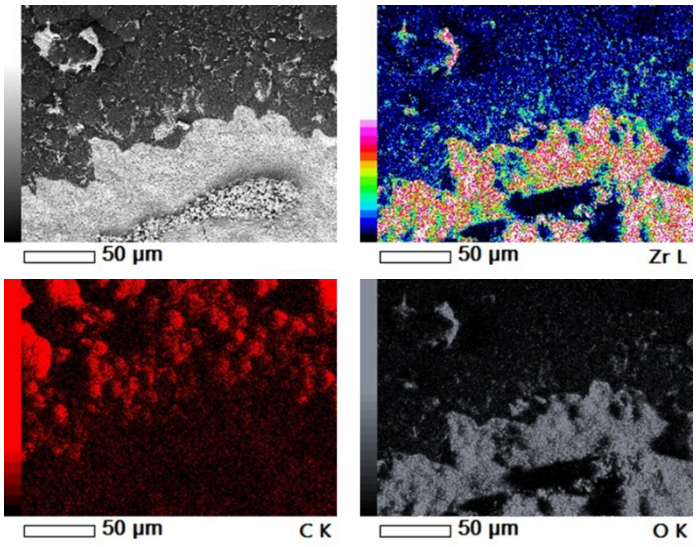

Fig. ESI 4. SEM micrograph of Zr coated graphite P1 and the corresponding EDX elemental mapping for Zr, C, and O taken at 5 kV. A ZrO atomic ratio of 1:2 was quantified by EDX standardless analysis.

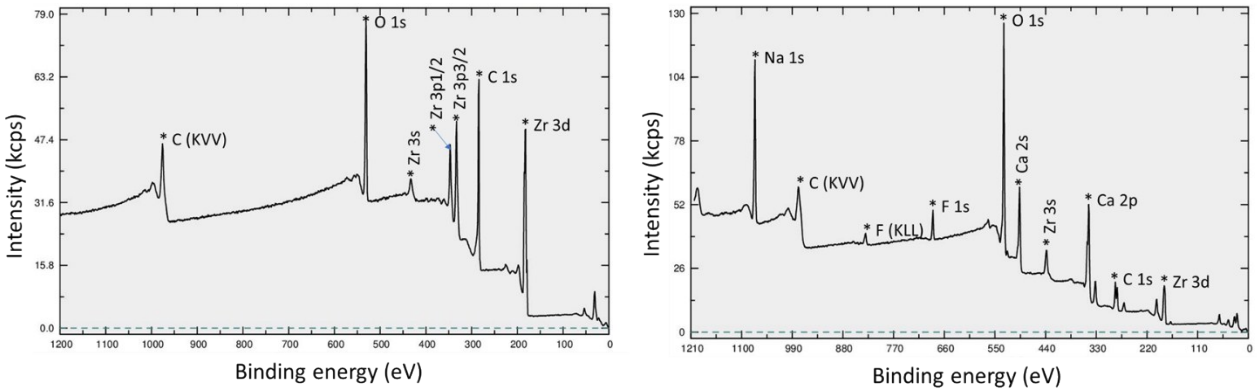

Fig. ESI 5. (Left) Wide scan XPS of a zirconium-coated platform P1. (Right) Wide scan XPS of the transition state P2: a zirconium coated platform after pyrolysis of NaF and $Ca(NO_3)_2$ at 900 °C.

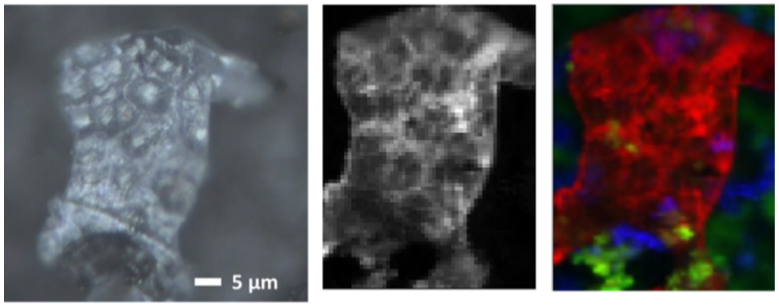

Fig. ESI 6. (Left) A micrograph of a zirconium-coated graphite platform after atomisation (P3) and its corresponding Raman mapping (middle) at characteristic Raman shift 273.82 cm^{-1} of ZrO_2. (Right) in red is represented ZrO_2 and evidence of graphite degradation due the calcium atomisation: in green is mapped the Raman shift 1,096.15 cm^{-1} corresponding to $CaCO_3$ and in blue is represented the Raman shift at 1,517.83 cm^{-1} of amorphous carbon.

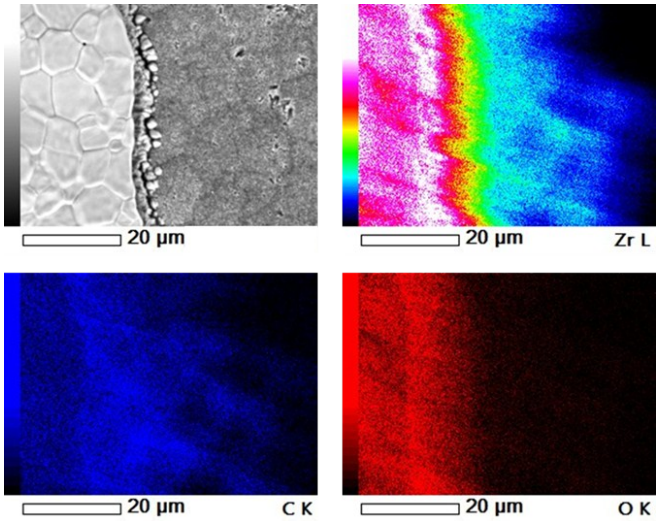

Fig. ESI 7. SEM micrograph of Zr-nano coated graphite and the corresponding EDX elemental mapping for Zr, C, and O taken at 5 kV. A ZrO atomic ratio of 1:2 was quantified by EDX standardless analysis.

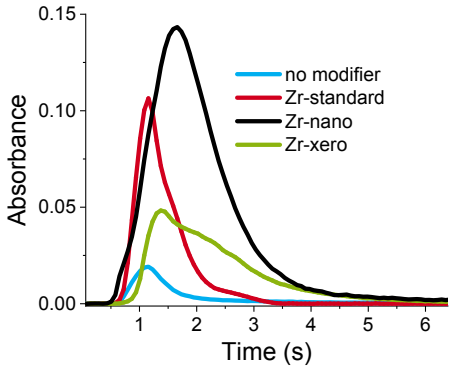

Fig. ESI 8. The effect on the preparation of ZrO modified graphite platforms on the analytical signal of CaF in HR-CS-MAS.

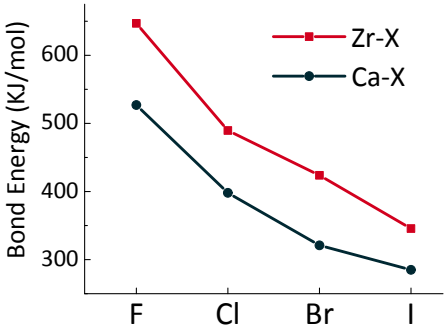

Fig. ESI 9. Tendency of bond strength for zirconium and calcium halogenides.[1]

Table ESI 1. Temperature programs used for CaX molecular absorption in the graphite furnace (X = F, Cl, Br, I)

CaX (Wavelength/nm)	F (606.4347)	Cl (618.4340)	Br (625.3150)	I (638.9195)	Heating rate	Holding time
Step					(°C s^{-1})	(s)
Drying 1	90	90	90	90	10	20
Drying 2	130	130	130	130	2	10
Pyrolysis	900	700	800	800	100	20
CaX vaporization	2300	2100	2400	2400	2000	10
Clean out	2600	2600	2600	2600	1000	3

Reference

1. Bond Energies. In Encyclopedia of Inorganic Chemistry, King, R. B.; Crabtree, R. H.; Lukehart, C. M.; Atwood, D. A.; Scott, R. A., Eds. John Wiley & Sons, Ltd: 2006.