

Supplementary information

Kinetic model

There are different techniques to study the solid-state kinetics, which are classified into two main categories: model fitting and model-free methods. The model-free methods can determine the apparent activation energy, without prior knowledge of the reaction order, by determination of the oxidation temperature required for a fixed conversion value (α) at different heating rates (β). These methods allow the kinetic parameters of a solid-state reaction to be obtained.

The conversion, α , was calculated by the following equation:

$$\alpha = \frac{m_t - m_i}{m_f - m_i} \quad (\text{S1})$$

where m_i is the initial mass, m_t is the mass at the instant t and m_f is the final mass after oxidation.

The reaction rate, $d\alpha/dt$, of a solid-state process can be related to that process temperature, as follows [1]:

$$\frac{d\alpha}{dt} = A(\alpha)f(\alpha)\exp\left(\frac{-E(\alpha)}{RT}\right) \quad (\text{S2})$$

where E_a is the activation energy (kJ mol^{-1}), T is the absolute temperature (K), R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and A is the pre-exponential factor (min^{-1}). The combination of the two equations provides the fundamental expression of analytical methods to calculate kinetic parameters.

Model-free methods

Flynn-Wall-Ozawa method

The FWO method allows the apparent activation energy (E_α) to be obtained from the plot of the natural logarithm of heating rates, $\ln\beta_i$, versus $1000/T_{\alpha i}$, which represents the linear relation for a given value of conversion, α , at different heating rates [1]:

$$\ln(\beta_i) = \ln\left(\frac{A_\alpha E_\alpha}{Rg(\alpha)}\right) - 5.331 - 1.052\frac{E_\alpha}{RT_{\alpha i}} \quad (S3)$$

where $g(\alpha)$ is the integral function of conversion. The subscripts i and α denote the given value of heating rate and the given value of conversion, respectively. The activation energy, E_α , is calculated from the slope $-1.052E_\alpha/R$ [1].

Kissing-Akahira-Sunose (KAS)

The KAS method is based on the following expression:

$$\ln\left(\frac{\beta_i}{T_{\alpha i}^2}\right) = \ln\left(\frac{A_\alpha R}{E_\alpha g(\alpha)}\right) - \frac{E_\alpha}{RT_{\alpha i}} \quad (S4)$$

The apparent activation energy can be obtained from a plot of $\ln\left(\frac{\beta_i}{T_{\alpha i}^2}\right)$ versus $1000/T$ for a given value of conversion, α , where the slope is equal $-E_\alpha/R$ [1].

Model based methods

The model-based methods allow the determination of the reaction mechanism by the minimization of the differences between experimental and calculated values. Accordingly, the function $f(\alpha)$ is used to describe the rate limiting, mechanistic reaction, Table 2, which is chosen from a row of tabulated functions based on the data obtained from a preliminary model-free estimation [2].

Table 2 – Most common algebraic expression for the $f(\alpha)$ function to describe solid-state reactions[2].

Mechanism	Symbol	$f(\alpha)$
Phase boundary-controlled reaction (bidimensional shape)	R2	$(1 - \alpha)^{\frac{1}{2}}$
Phase boundary-controlled reaction (tridimensional shape)	R3	$(1 - \alpha)^{\frac{2}{3}}$
N order reaction	Fn	$(1 - \alpha)^n$
Unimolecular decay law (instantaneous nucleation and unidimensional growth)	F1	$(1 - \alpha)$
Random instant nucleation and two-dimensional growth of nuclei (Avrami-Erofeev equation)	A2	$2.079(1 - \alpha)^{0.806}\alpha^{0.515}$
Random instant nucleation and three-dimensional growth of nuclei (Avrami-Erofeev equation)	A3	$3.192(1 - \alpha)^{0.748}\alpha^{0.693}$
Two-dimensional diffusion (bidimensional particle shape)	D2	$0.973(1 - \alpha)^{0.425}\alpha^{-1.008}$
Three-dimensional diffusion (tridimensional particle shape)	D3	$4.431(1 - \alpha)^{0.951}\alpha^{-1.004}$

Therefore, the result of the model-based analysis provides information about the reaction mechanism, the form of equations for the elementary stages and the values of the kinetic triplets (A , E_a and $f(\alpha)$) for these stages. The model-based kinetic analysis was performed *NETZSCH Kinetics Neo* and can be based on models which include several process steps, in which the individual steps are linked as independent, parallel, competing or following reactions. Each, model selected, reaction type for each step has some unknown kinetic parameters such as activation energy, pre-exponential factor, reaction order as well as the contribution of each step to the overall process. All unknown parameters can be found from the fit of the measured data with the simulated curves. Statistical comparison of fit for different models allows to select the appropriate model with a corresponding set of parameters [3].

Thermogravimetric analysis (TGA)

A combination of thermogravimetric (TGA) and elemental chemical analysis studies was performed to estimate the oxygen and nitrogen contents incorporated into the anionic sublattice of the compounds. To this goal, we first calculated the mass variation of the fully oxidised V_2O_5 precursor powder during heating at 600 °C in pure O_2 .

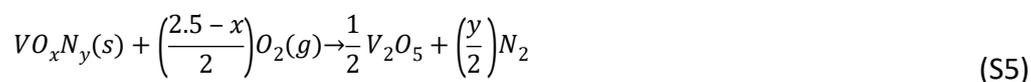


Fig.S1 exhibits the obtained TGA curves for the VON synthesized at 600 °C for different dwell times of 1, 4, 8 and 12h at 600 °C, showing that all the compositions exhibited similar behaviour. Nonetheless, the sample with lower synthesis dwell time, 1h, shows a slightly lower weight gain, suggesting that his sample has a higher O content and a lower N content, as confirmed by elemental analysis (Table S1). For the samples synthesized at 4h, 8h and 12h, the divergence of weight gain between samples is much lower, with the compounds possessing similar O/N contents in the anionic lattice when assessed by elemental analysis (see Table S1).

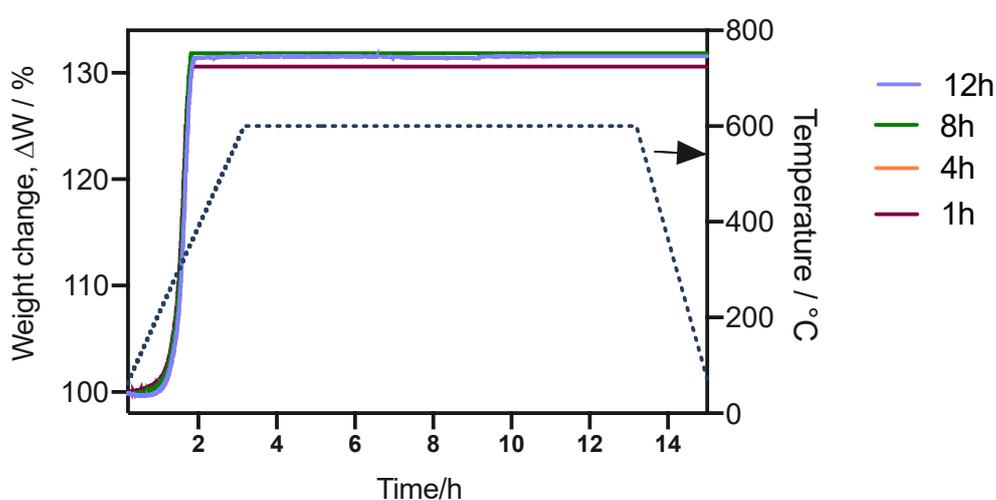


Fig. S1 – TGA of selected materials produced at different dwell times (1,4,8 and 12 hours at a fixed synthesis temperature of 600 °C) O₂ at 600 °C

The O contents measured experimentally by TGA (using Eq. S5) and the N contents determined by elemental analysis (normalized to a anion occupancy of unity) are shown in Table S1 for all the compounds synthesized in this work.

TableS1 – N content determined by chemical analysis and O content measured by TGA.

Ammonolysis temperature / °C	Dwell time/h	O content by TGA	N content by chemical analysis
600	1	0.37	0.63
600	4	0.30	0.70
600	8	0.31	0.69
600	12	0.30	0.70
700	12	0.22	0.78
800	12	0.10	0.90
900	12	0.08	0.92

1000	12	0.06	0.94
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Kinetic model

The kinetic parameters obtained by FWO and KAS plots, were determined for the selected compositions (Fig.S2), providing the activation energy and pre-exponential factors from subsequent linear regression.

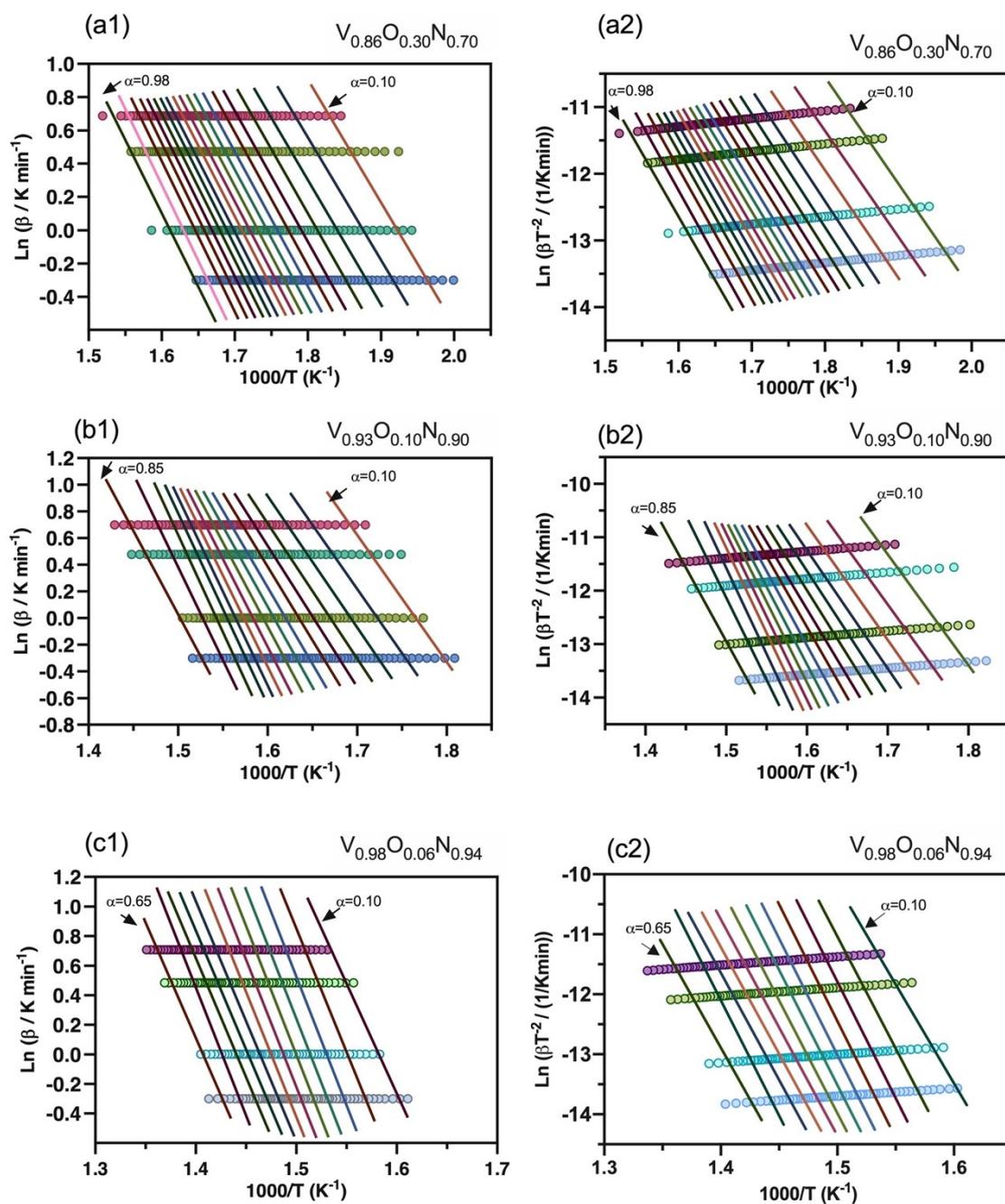


Fig. S2– (a1,b1,c1) FWO and (a2,b2,c2) KAS plots for $V_{0.86}O_{0.30}N_{0.70}$, $V_{0.93}O_{0.10}N_{0.90}$ and $V_{0.98}O_{0.06}N_{0.94}$ samples, respectively.

References

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