

SUPPLEMENTARY INFORMATION

Aqueous citrato-oxovanadate(IV) solutions for VO₂: synthesis, spectroscopic investigation and thermal analysis

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Spectroscopic investigation of the (NH₄)₂C₂O₄·xH₂O precipitate

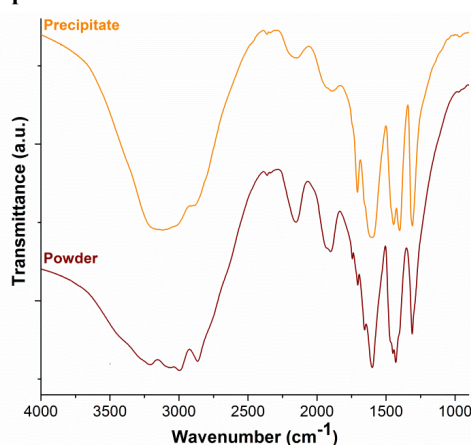


Figure S1: FTIR spectra of the precipitate originating from the synthesis of the aqueous citrato-VO²⁺ precursor solution, and the powder obtained from the vanadium free, ammonium oxalate solution.

Figure S1 shows the FTIR spectra of the precipitate, originating from the synthesis of the aqueous citrato-VO²⁺ precursor solution, and of the vanadium free, ammonium oxalate powder. The assignment of the main vibrations is given Table S2. Both infrared spectra show a strong absorption band between 3200 and 2800 cm⁻¹ due to the O-H stretching mode of the hydrates and the N-H stretching mode of the ammonium ion, broadened by H-bridge formation. Additional N-H stretching modes of the ammonium ion can be observed in both spectra at about 2150 and 1900 cm⁻¹. Typical carboxylate stretch vibrations in (NH₄)₂C₂O₄ appear at 1710, 1655 and 1605 cm⁻¹ for ν_{as}(COO⁻) and at 1450 and 1410 cm⁻¹ for ν_s(COO⁻).¹⁻⁴ Frost et al. explains the multiplicity of bands by the structural variety of oxalate species in ammonium oxalate (i.e. mono-, di- and polyoxalates).² Furthermore, the band at 1410 cm⁻¹ coincides with the ammonium deformation. The intense absorption peak observed at 1315 cm⁻¹ corresponds to the O-C=O deformation.¹⁻⁴ No vanadyl stretching mode, corresponding to ν(V⁴⁺=O) or ν(V⁵⁺=O), are observed around 960 or 1020 cm⁻¹.⁵

Precipitate	Powder		Assignment
3200-2800 (br.)	3200-2800 (br.)	ν(O-H) ν(N-H)	O-H stretching in hydrated H ₂ O N-H stretching in NH ₄ ⁺
2151	2160	ν(N-H)	N-H stretching in NH ₄ ⁺
1904	1900	ν(N-H)	N-H stretching in NH ₄ ⁺
1710	1702		
1655	1660	ν _{as} (CO ₂ ⁻)	Asymmetric CO ₂ ⁻ stretching
1607	1605		
1450	1460	ν _s (CO ₂ ⁻)	Symmetric CO ₂ ⁻ stretching
1400	1410		
1400	1410	δ(NH ₄ ⁺)	NH ₄ ⁺ deformation
1315	1313	δ(O-C=O)	O-C=O deformation

Table S2: Band assignments of the main vibrations (expressed in cm⁻¹) of the FTIR spectra of the precipitate, formed during the synthesis of the citrato-VO²⁺ solution, and the ammonium oxalate powder. The assignments are based on references¹⁻⁴.

Spectroscopic investigation of the citrato-oxalato-VO²⁺ and citrato-VO²⁺ gel

Gels of both solutions, obtained by drying at 60 °C, are analysed by FTIR Spectroscopy and compared to those of a VO²⁺-free ammonium citrate gel in Figure S3. A full assignment of the measured absorption bands is reported in Table S4. All spectra show a strong absorption band between 3400 and 2800 cm⁻¹ due to (i) the O-H stretching mode of H-bonded hydroxyl groups and absorbed H₂O molecules, (ii) the N-H stretching mode of the ammonium ions and (iii) the C-H stretching mode of the citrate's methylene bridges.³⁻⁵ These absorption bands are broadened by H-bridge formation. For the typical asymmetric and symmetric carboxylate stretch vibrations, differences in the citrato-oxalato-VO²⁺ and the citrato-VO²⁺ precursor gels are observed. In the presence of oxalate, a first ν_{as}(CO₂⁻) appears at 1710 cm⁻¹ and is associated with the ammonium oxalate present in the citrato-oxalato-VO²⁺ precursor.² Both the citrato-VO²⁺ precursor gel and the gel of the VO²⁺-free ammonium citrate solution have no clear vibration peak at this position. However, in all spectra a similar ν_{as}(CO₂⁻) arises around 1590 cm⁻¹ and is assigned to asymmetric stretch vibrations in the carboxylate groups interacting with (i) VO²⁺ in the citrato-oxalato-VO²⁺ and the citrato-VO²⁺ precursor gel and (ii) the ammonium ion in all the studied gels.³⁻⁵ Again in the presence of oxalate, a first ν_s(CO₂⁻)

appears at 1441 cm^{-1} and is associated with the ammonium oxalate present in the citrato-oxalato- VO^{2+} precursor solution.² In the spectra a clear $\nu_s(\text{CO}_2^-)$ appears around 1400 cm^{-1} and is assigned to a symmetric stretch vibration of the carboxylate groups interacting with VO^{2+} in the citrato-oxalato- VO^{2+} and the citrato- VO^{2+} precursor gel.²⁻⁴ The peak at 1400 cm^{-1} coincides with that of the ammonium deformation, which explains its presence in the spectrum of the VO^{2+} -free ammonium citrate gel. In all spectra, two peaks assigned to the C-O stretching mode in C-OH are observed around 1120 and 1070 cm^{-1} .²⁻⁴ The vanadyl stretching mode, $\nu(\text{V}^{4+}=\text{O})$, is observed in the gels associated with the citrato-oxalato- VO^{2+} and the citrato- VO^{2+} precursor solution at 960 cm^{-1} , indicating the presence of the oxovanadate species in each precursor solution.⁶ Moreover, the absence of VO_2^+ species is supported by the absence of the $\nu(\text{V}^{5+}=\text{O})$ stretching mode around 1020 cm^{-1} .⁵ In conclusion, the presence of the citrato- VO^{2+} complexes and the ammonium groups linking the excess citrate, is suggested by the FTIR spectra of the citrato-oxalato- VO^{2+} and citrato- VO^{2+} precursor gels. Vibrations owing to the oxalate residues are observed in the spectra of the citrato-oxalato- VO^{2+} precursor gel, but not in the citrato- VO^{2+} precursor gel, which proofs that oxalate is indeed removed during the precipitation step in the synthesis of the oxalate-poor citrato- VO^{2+} solution.

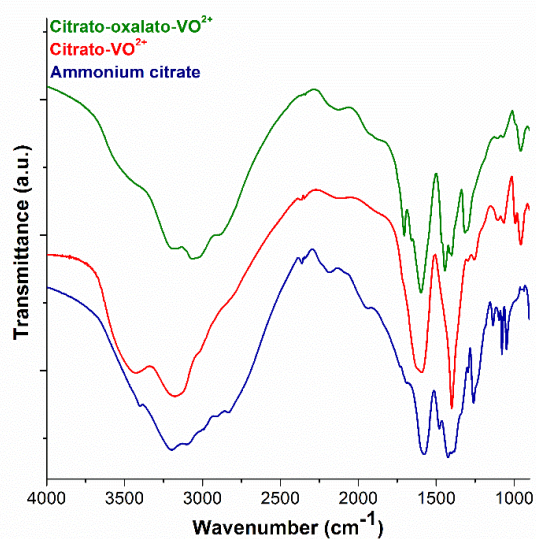


Figure S3: FTIR spectra of gels of the aqueous citrato-oxalato- VO_2^+ , citrato- VO_2^+ and ammonium citrate solutions obtained after drying at 60 °C.

(1)	(2)	(3)	Assignment	
3400-2800 (br.)	3400-2800 (br.)	3400-2800 (br.)	$\nu(\text{O-H})$	O-H stretching in C-OH and H_2O
			$\nu(\text{N-H})$	N-H stretching in NH_4^+
			$\nu(\text{C-H})$	C-H stretching in CH_2
2142 1902	2153 1907	2150 1904	$\nu(\text{N-H})$	N-H stretching in NH_4^+
1708	-	-	$\nu_{\text{as}}(\text{CO}_2^-)$	Asymmetric CO_2^- stretching in $(\text{NH}_4)_2\text{C}_2\text{O}_4$
1595	1587	1594	$\nu_{\text{as}}(\text{CO}_2^-)$	Asymmetric CO_2^- stretching interacting with VO^{2+} and/or NH_4^+
1441	-	-	$\nu_s(\text{CO}_2^-)$	Symmetric CO_2^- stretching in $(\text{NH}_4)_2\text{C}_2\text{O}_4$
1400	1402	1402	$\nu_s(\text{CO}_2^-)$	Symmetric CO_2^- stretching interacting with VO^{2+}
1119 1076	1115 1067	1138 1078	$\delta(\text{NH}_4^+)$	NH_4^+ deformation
			$\nu(\text{C-O})$	C-O stretching in C-OH doublet
960	960	-	$\nu(\text{V}^{4+}=\text{O})$	$\text{V}^{4+}=\text{O}$ stretching

Table S4: Band assignments of the main vibrations (expressed in cm^{-1}) of the FTIR spectra of the citrato-oxalato- VO^{2+} (1) citrato- VO^{2+} (2) and VO^{2+} -free ammonium citrate (3) gels. The assignments are based on references¹⁻⁵.

References

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