Vanadium Oxide-based electrochromic devices for display applications

By

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Highlights

Electrochromism

- Vanadium oxides (VO) shows electrochromism
- Thin films with macroporous crystalline *nanosheets*
- Unconventional colour change

Yellow ↔ *Green* ↔ *Grey*

- Li-free, ecofriendly, cheaper electrolyte – *Salt based*
- VO devices that works on *FTO* as counter electrode
- VO as both anodic and cathodic

Summary

- DC magnetron sputtering › Amorphous V_2O_5
- Post-annealing to 400 °C shows a change in properties
- Phase transition: Amorphous to macroporous crystalline V_2O_5

Sample: Δ @400 °C			
D_{av} (nm)	65.8 ± 12	R_a (nm)	26.5
ε	0.0032	SEM (nm)	169
δ (lines/m²)	4.6 x 10^{14}	E_g (eV)	2.78

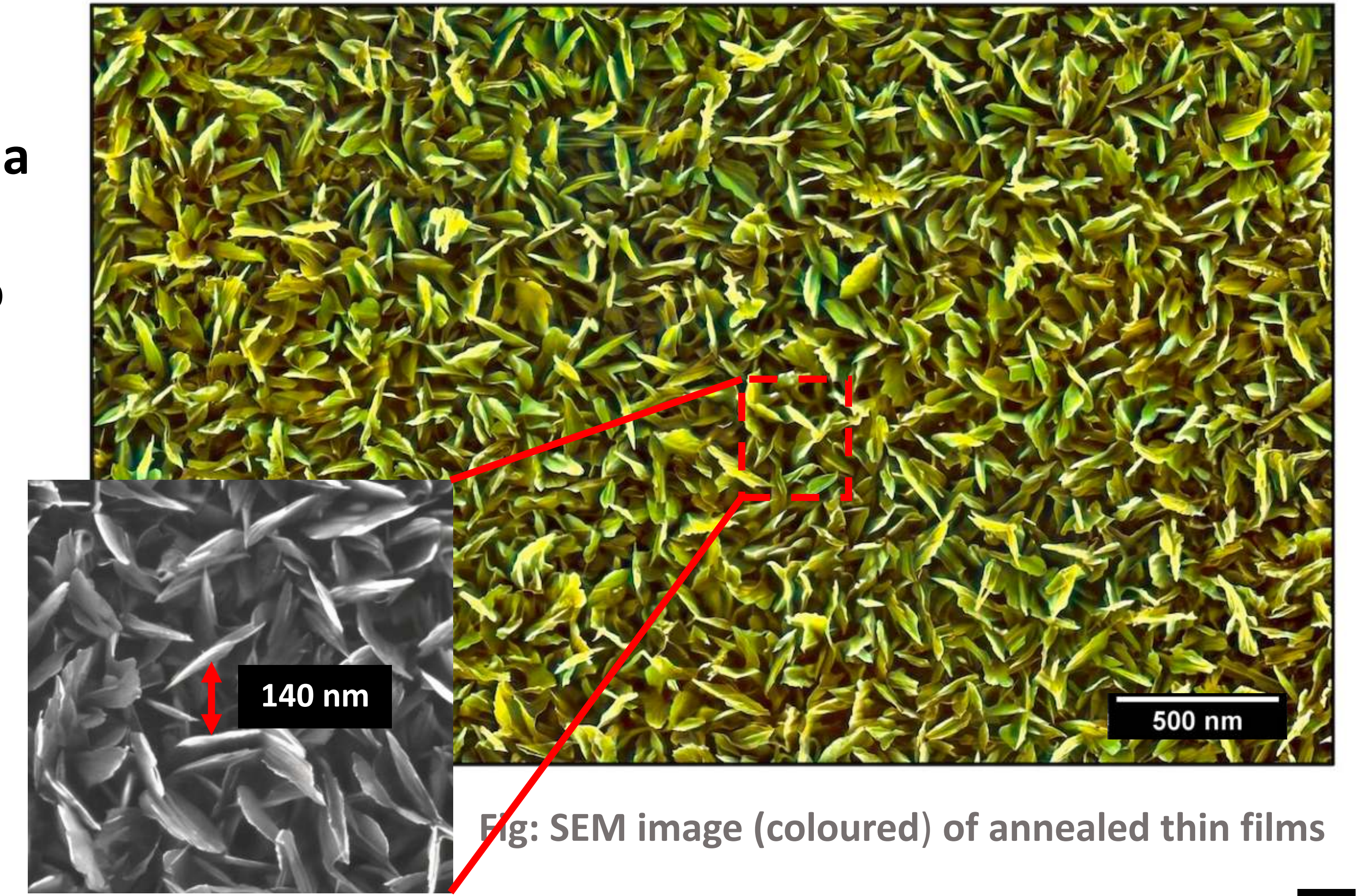
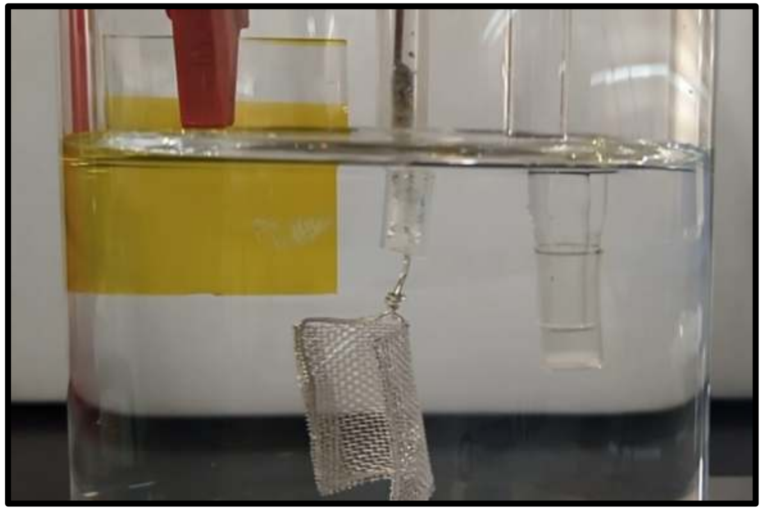


Fig: SEM image (coloured) of annealed thin films

Ranjithvel M, Grasslands of Shcherbinaite : A Metamorphosis Chronicle, ASM Metallography contest in Amalgam 2024, 1-3 March 2024, IIT Madras Chennai - 600036, India (Micrography-Second prize)

Electrochemical setup

- Salt-based electrolytes: 1M NaCl, KCl and $CaCl_2$
- Potential window: ± 1 V
- Scan rate: 10 mVs^{-1}
- Thickness of film: 80 ± 2 nm



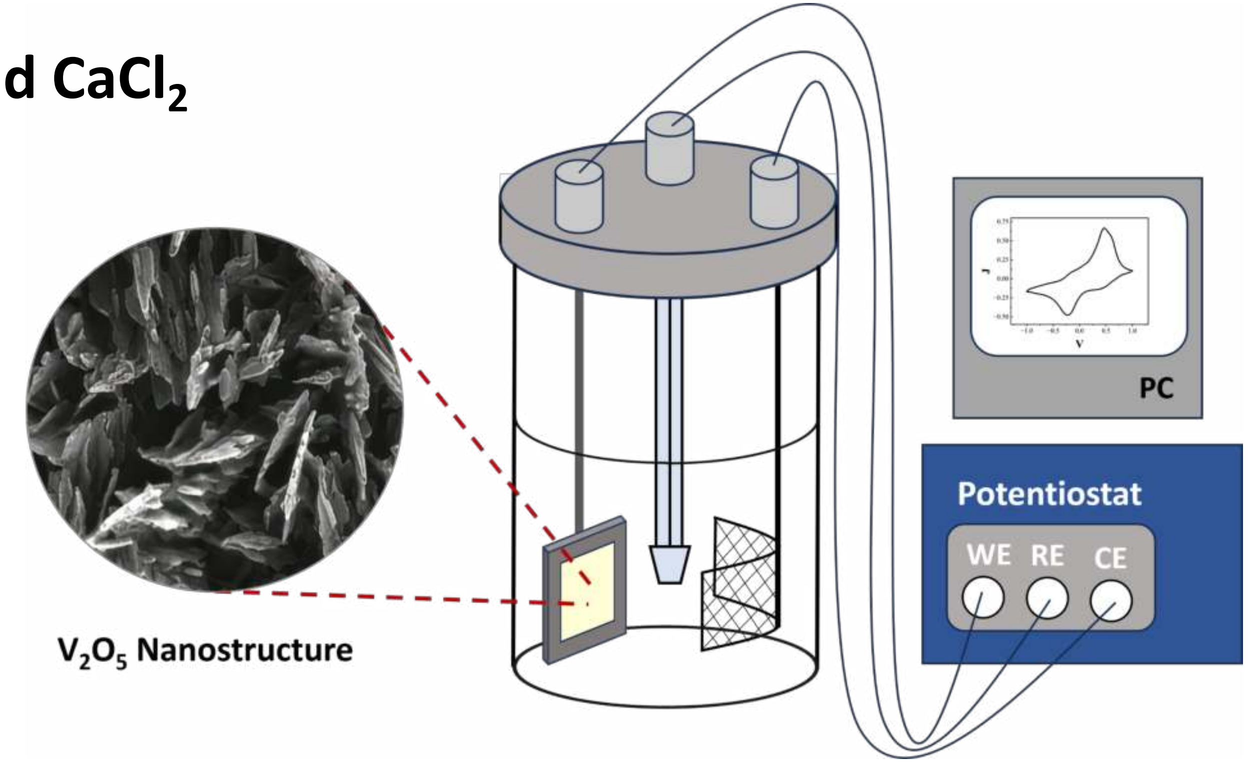


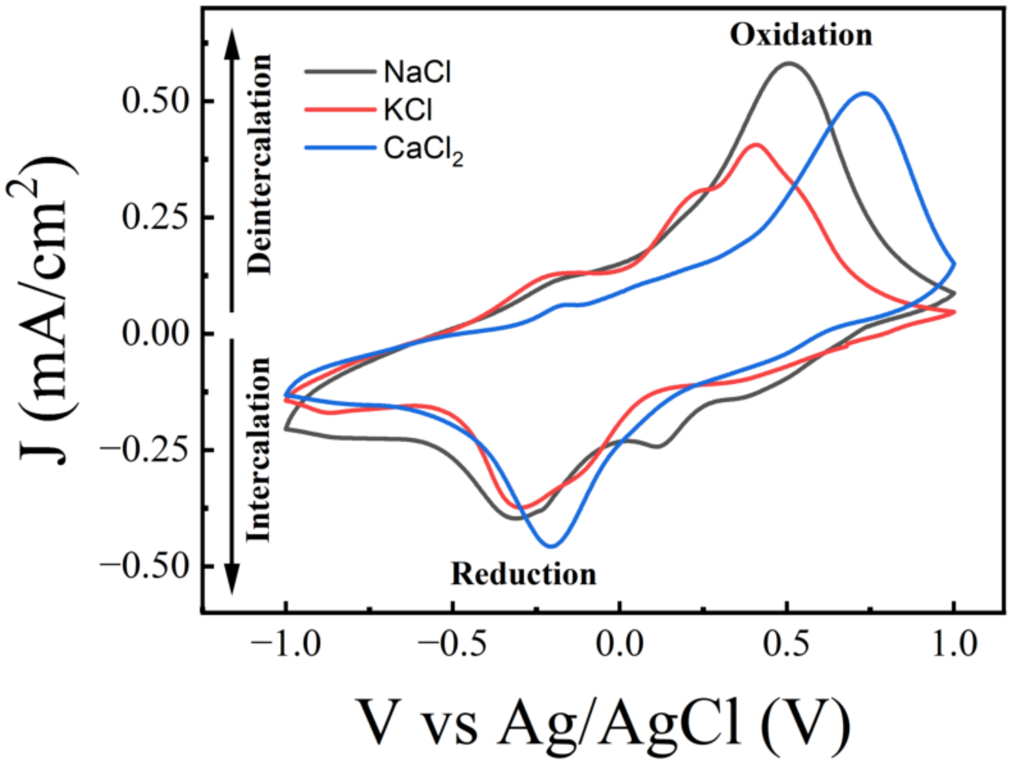
Fig: Electrochemical three electrode setup

Reversible color change due to double injection of electrons and metal cations.

$$\boxed{V_2O_5 + xM^+ + xe^- \rightleftarrows M_xV_2O_5}$$

M^+ = metal cations (Na^+, K^+, Ca^{2+})

Cyclic voltammetry



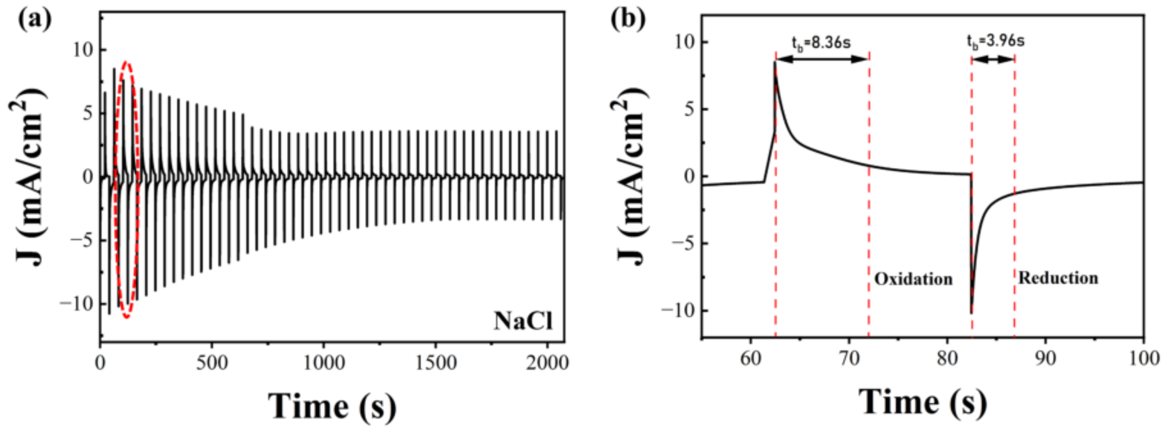
Electrolyte	V_p (V)		J ($mAcm^{-2}$)		*D (10^{-10} cm^2s^{-1})	
	V_{pa}	V_{pc}	J_{pa}	J_{pc}	D_a	D_c
NaCl	0.53	-0.31	0.58	-0.39	4.66	2.18
KCl	0.40	-0.33	0.41	-0.37	2.37	1.97
$CaCl_2$	0.73	-0.21	0.52	-0.46	0.46	0.36

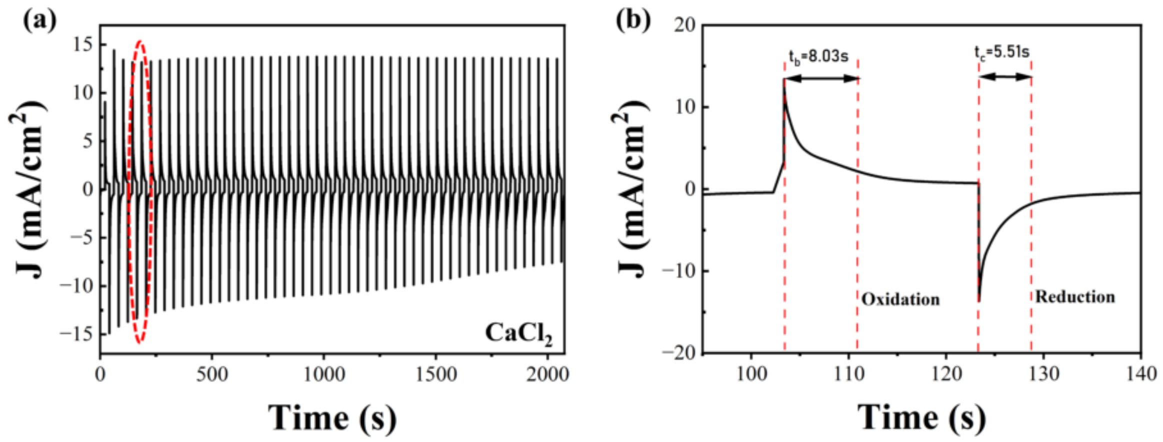
- Wide operating voltage for $CaCl_2$
- Slower diffusion rates found in $CaCl_2$
- Lower D due to larger ionic size as well as higher valency

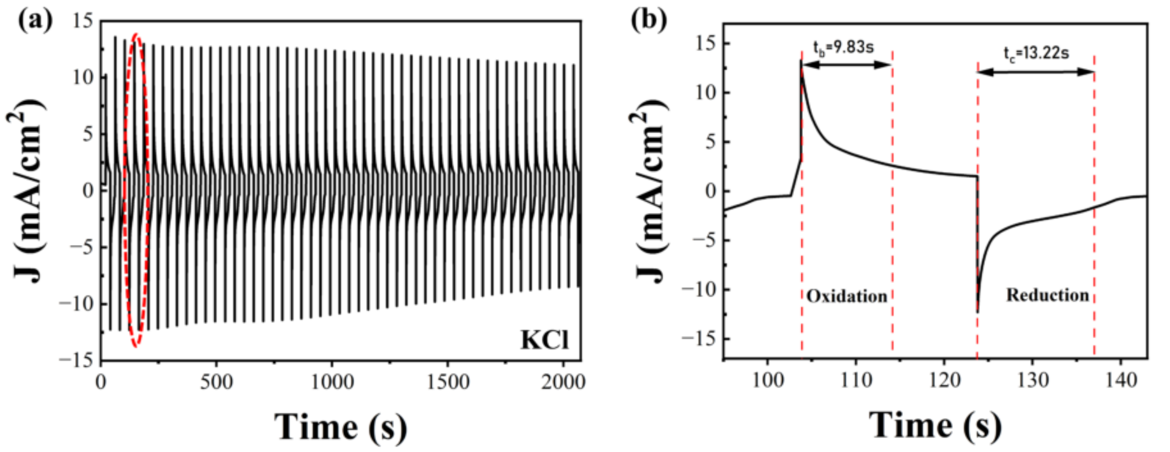
*Randell Schvik equation used to find diffusion coefficient

Na^+(0.095 nm) < Ca^{2+}(0.1nm) < K^+(0.133nm)

Chronoamperometry



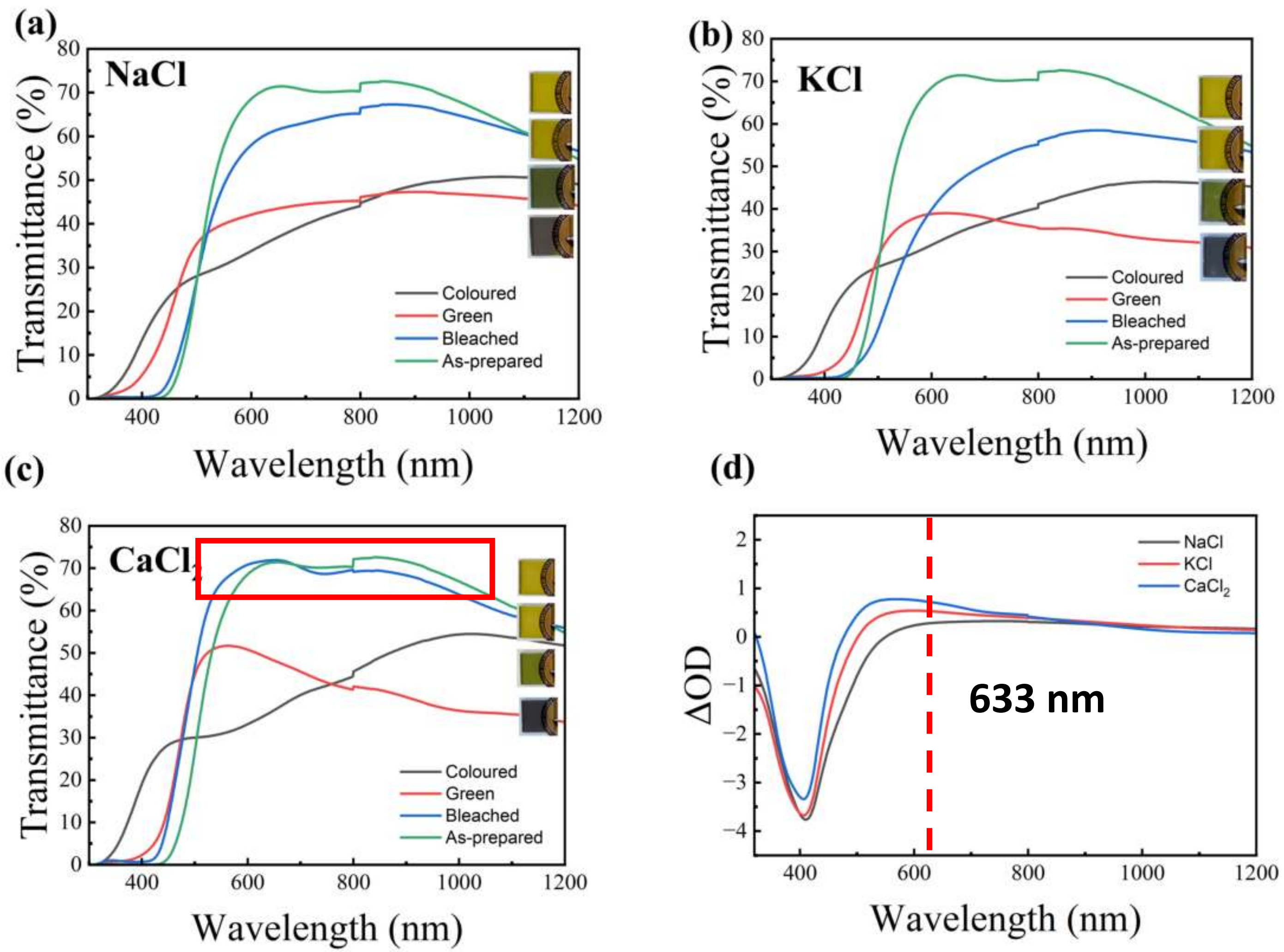




- **K^+ ions take longer time to intercalate whereas others take more time for deintercalation**
- **Intercalation/Deintercalation is faster in Na^+ and Ca^{2+} ions**
- **Better stability is seen in KCl and $CaCl_2$**

$CaCl_2$ exhibits both faster response as well as long term stability

UV-VIS spectroscopy



Electrolyte	Transmittance (%)		ΔT (%)
	T_{ox}	T_{red}	
NaCl	44.3	33.3	11.0
KCl	60.6	35.8	24.8
$CaCl_2$	71.7	35.1	36.6

- **Also, the color change in $CaCl_2$ electrolyte is fully reversible to annealed sample**

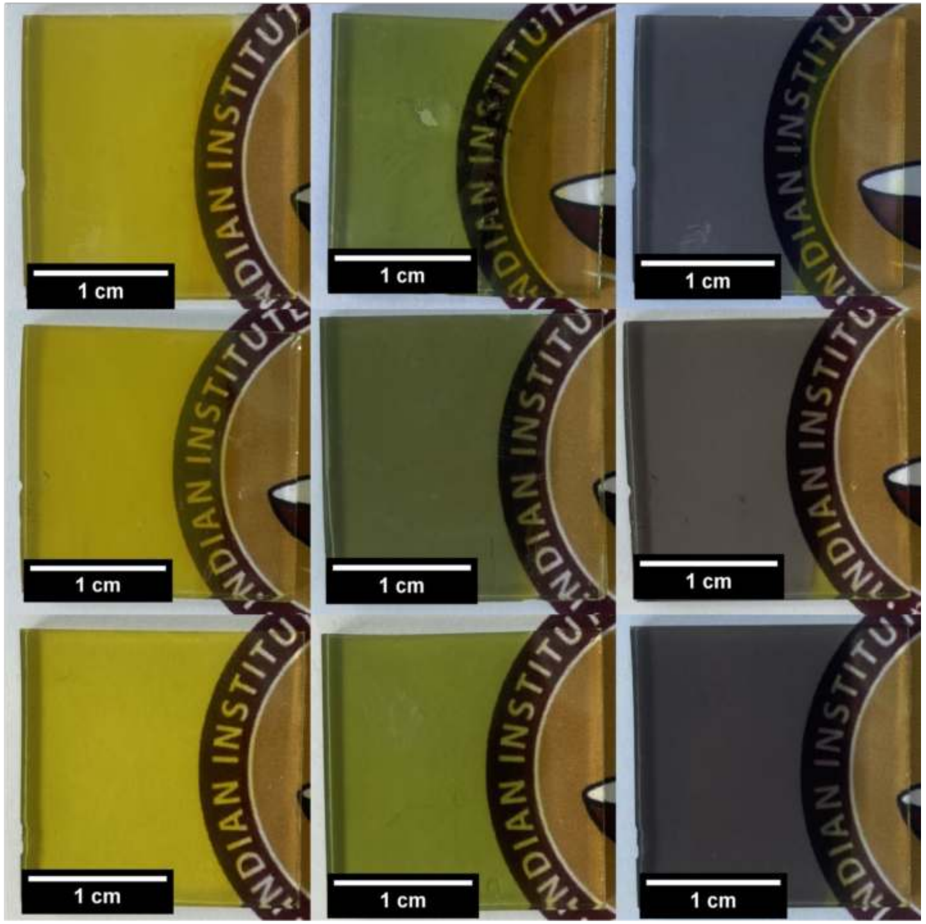
Visual aspect - Colorimeter

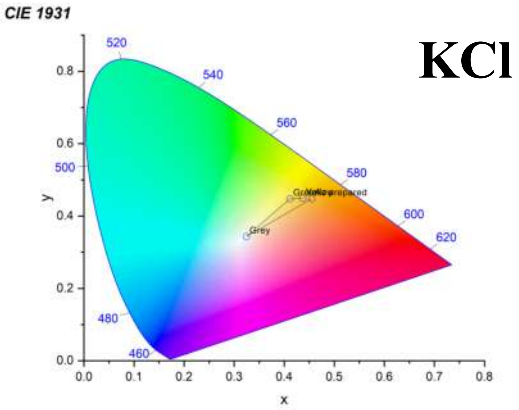
Potential → +0.6 V -0.2 V -0.5 V

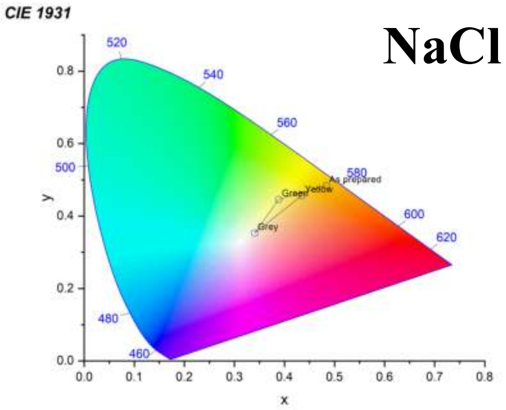
NaCl

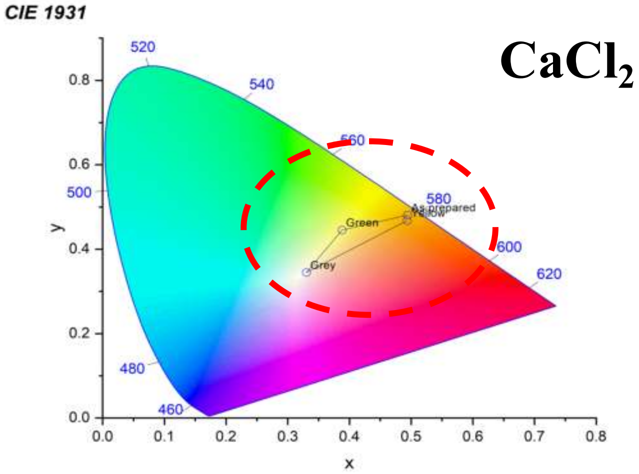
KCl

$CaCl_2$









Yellow(V^{5+}) ↔ Green (V^{4+}) ↔ Grey (V^{3+})

Best colour contrast and reversibility

Conclusions

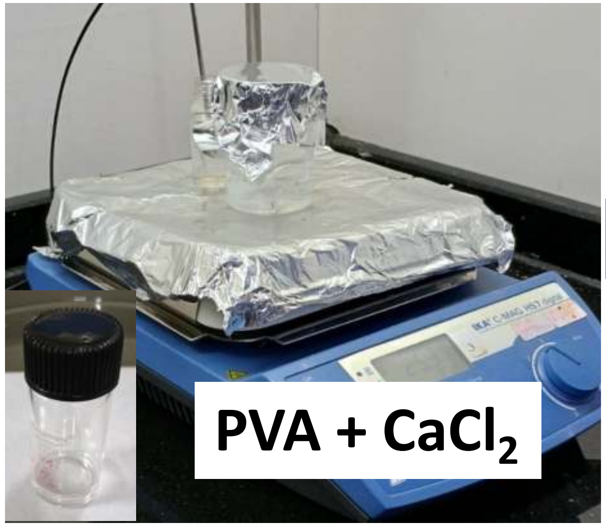
Electrolyte	Q (mC cm^{-2})		ΔT (%)	ΔOD	η (cm^{2}C^{-1})	t_a (s)	R (%)	PI
	Q_{ox}	Q_{red}						
NaCl	32.12	36.05	11.0	0.284	7.88	6.16	89	1.28
KCl	23.36	28.84	24.8	0.527	18.27	11.52	81	1.58
$CaCl_2$	26.80	28.43	36.6	0.715	25.14	6.77	94	3.71

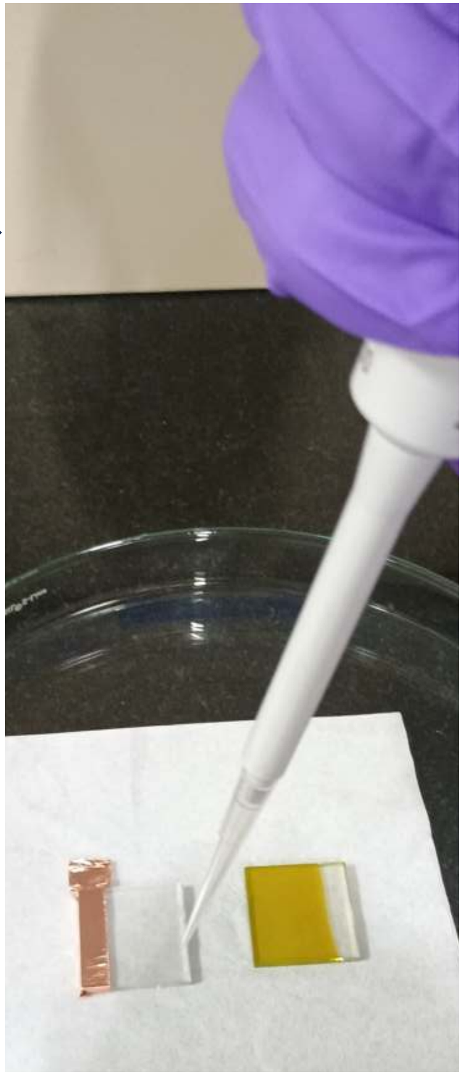
- **Nanosheets are found to be well suited for EC behaviour**
- **Higher stability is due to lower ion trapping <= shallow level intercalation (diffusion length) and lower structural change**
- **Larger ΔT due to more number of electroactive sites – size effect (optimal size) and valency effect (more electron transfer)**
- **Salt based electrolytes are better alternatives to Li-electrolytes**

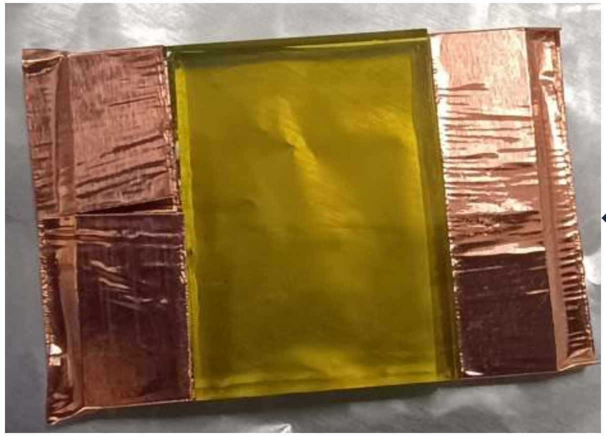
Comparison with literature

S.No.	Film structure	Thickness (nm)	Method of fabrication	Electrolyte	ΔT %	t_b/t_c (s)	η cm^2C^{-1}	Reference
1	Nanorods	723	Sol-gel	$LiClO_4$-PC	73.6	3.4/3.6	19.76	Liu et al., 2022
2	Inverse opal-2D	-	Electro deposition	$LiClO_4$-PC	42.6	7.2/2.5	28.6	Zhao et al., 2022
3	V_2O_5/ Graphene	360	Electro Deposition	$LiClO_4$-PC	32.54	6.2/7.9	19.77	Li et al., 2024
4	V_2O_5:WO_3	421	RF sputtering	$LiClO_4$	41.7	1.4/5.5	-	Mehmood et al., 2021
5	V_2O_5	-	Ultrasonic spray	$LiPO_4$	17	-	-	Tutel et al., 2021
6	P.V_2O_5	118	Spray Pyrolysis	$LiClO_4$	25	-	13	Patil et al., 2009
7	V_2O_5 Nanobelts	800	Solution Processed	$LiClO_4$ PMMA-PC	41.6	4.2/1.4	83.3	Zhang et al., 2020
8	V_2O_5 Nanosheet	80	Magnetron Sputtered	NaCl	11	8.36/3.96	7.9	This work
				KCl	24.8	9.83/13.22	18.27	
				$CaCl_2$	36.6	8.03/5.51	25.14	

Solid state device preparation







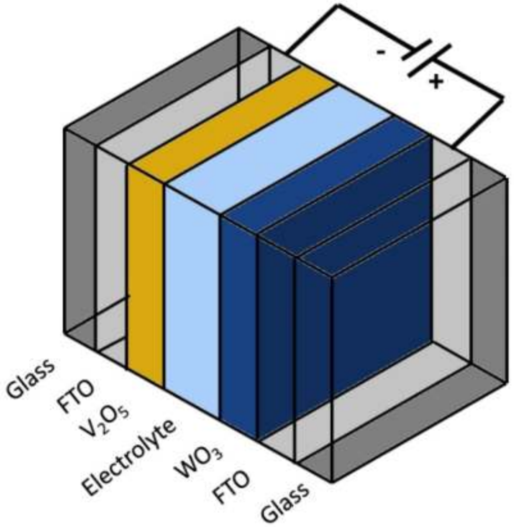
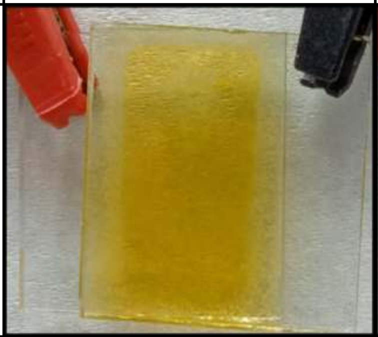
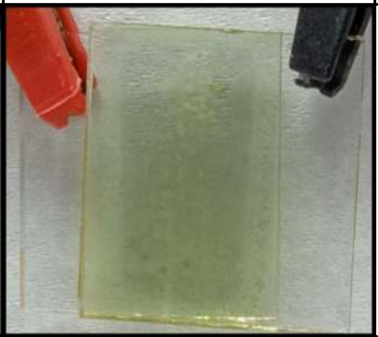
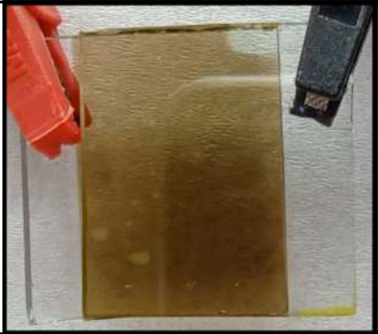
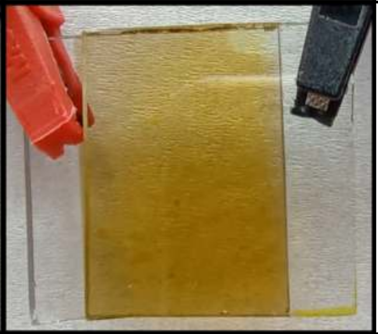
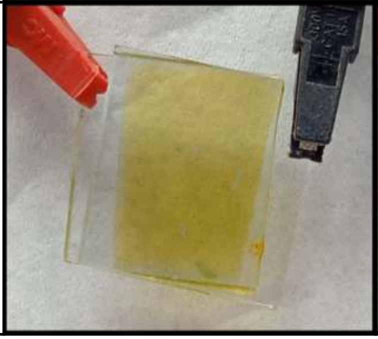
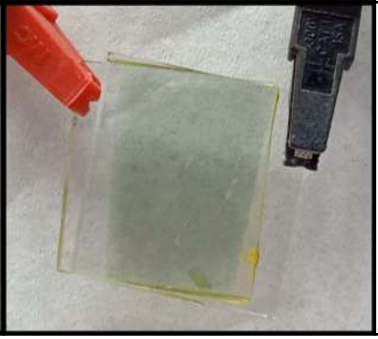
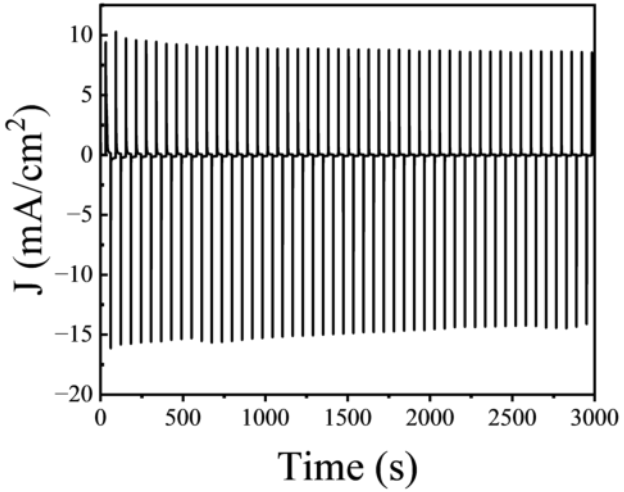


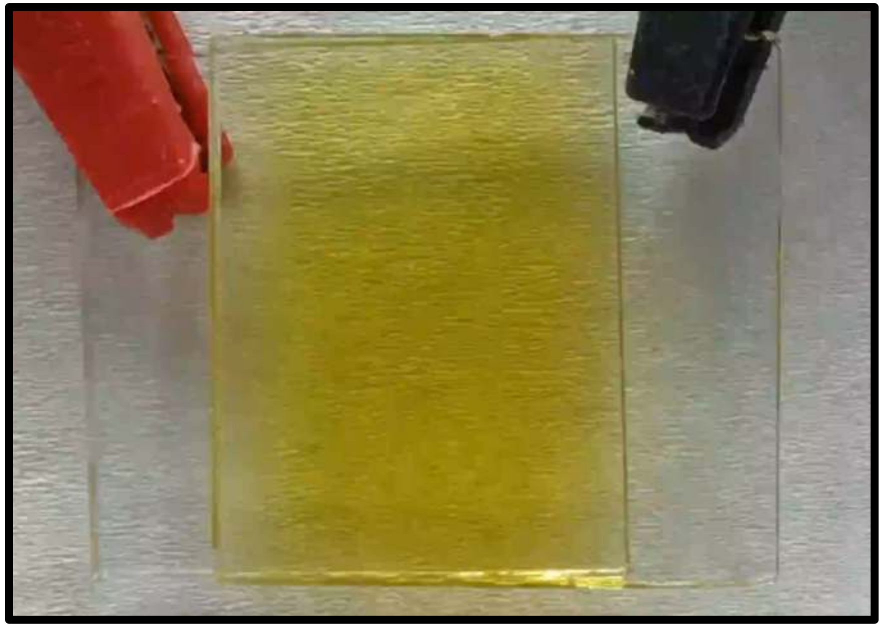
Fig: Typical structure of EC device

- **Curing the device at 45 °C for 2 hours**
- **No reports so far, using plain FTO as counter electrode**

Device performance

CE	+2 V	-2 V	t_c(s)	t_b(s)
FTO			5.46	5.02
NiO			3.27	1
WO_3			2.13	1.72





Future scope

- Making device on flexible substrates
- Composites of V_2O_5 – Doping to improve properties
- Study of devices on harsh environments
- Commercialization of devices
- Device integration – Ca-ion batteries, supercapacitors, sensors etc…

Visible output and acknowledgments

- **Ranjithvel M**, A. Sudha, A Ashok, S K Yadav and Parasuraman Swaminathan, **Magnetron sputtered vanadium oxide for electrochromic applications**, XXII International Workshop on the Physics of Semiconductor Devices (IWPSD 2023), 14-17 December 2023, Research Park, IIT Madras Chennai-600036, India (Poster).
- **Ranjithvel M**, A. Sudha, and Parasuraman Swaminathan, **Electrochromic behaviour of vanadium pentoxide on different electrolytes**, Amalgam 2024, 1-3 March 2024, IIT Madras Chennai-600036, India (oral).
- **Ranjithvel M, Grasslands of Shcherbinaite: A Metamorphosis Chronicle**, ASM Metallography contest in Amalgam 2024, 1-3 March 2024, IIT Madras Chennai - 600036, India (Micrography-Second prize).
- **Ranjithvel M**, A. Sudha, and Parasuraman Swaminathan, **Study of salt-based electrolytes on the electrochromic behaviour of sputtered vanadium pentoxide films**, (Manuscript to be submitted to the journal).

Thank you