ELECTRONIC SUPPORTING INFORMATION

MoO_x-based high-density nanoarrays on a substrate via smart anodizing as novel 3D electrodes for nano-energy applications

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Fig. S1. Voltage-time and current-time responses during: (a) the anodizing of an Al(800 nm)/Nb(25 nm)/Mo(170 nm)/SiO₂ trilayer in 0.6 M $H_2C_2O_4$ (oxalic acid) followed by re-anodizing in 0.5 M H_3BO_3 and 0.05 M $Na_7B_4O_7$ (borate buffer) up to 275 V; (b) the anodizing of the same trilayer in 0.6 M $H_2C_2O_4$ (oxalic acid) followed by re-anodizing in the borate buffer up to a maximum possible voltage (306 V); (c) the anodizing of the same trilayer in 0.2 M H_3PO_4 (phosphoric acid) at a steady-state voltage of 150 V immediately followed by re-anodizing in the same electrolyte without a break up to 160 V.

Elucidating the inner film structure and interfaces for quantitative analysis



Fig. S2. SEM cross-sectional images of the (a) OX48 PAA-inbuilt sample and (b, c) OX48-180 PAA-inbuilt sample.



Fig. S3. SEM cross-sectional images of the PAA-inbuilt samples (a) OX48, (b) OX48-150, (c) OX48-180, and (d) OX48-220. The image in panel (e) shows the PAA-free OX48-220 sample. The yellow dashed line marks the Mo/SiO₂ interface. The blue lines indicate the development of the nanostructured and bottom anodic oxides with increasing re-anodizing voltage.

XPS supplementary information

Nb 3d loss peak deconvolution

The fitting of the Mo 3d spectra was complicated by an overlap with the Nb 3d loss peaks at 221–227 eV. Their intensity was proportional to the intensity of the corresponding Nb 3d peaks, as seen in the combined Mo 3d + Nb 3d spectra of various metallic and anodic films with Mo content ranging between 0 and 35 at.% (when at.%(Mo+Nb) = 100 at.%, Fig. S4, left column). Inspired by the spectra of the low-Mo-content films (i.e., the pure Nb and OX48 films), we selected the 218–231 eV range for deconvoluting the Nb 3d loss contributions. The low-energy edge of the range (218 eV) may be too arbitrary since the intensity steadily increases from the edge of the Nb 3d peaks at around 212 eV. However, if the Nb 3d loss part of all the Mo-Nb-based samples is deconvoluted similarly, the result (mainly the Mo content) should be comparable for the samples. The ratio of the areas below the Nb 3d loss (~218–231 eV) and Nb 3d (~200–211 eV) peaks was 0.09±0.01 for the two low-Mo-content films; however, it was 0.175±0.02 for the higher-Mo-content films, i.e., above ~10 at.% Mo (~25 samples), although the same range was used for deconvoluting the Nb 3d loss peaks. We attribute such a difference to the fact that the background is established differently below the high-BE part of the Nb 3d loss peaks in the case when a relatively higher amount of Mo is present in the film, as seen in Fig. S4, right column.

The Nb 3d loss range was deconvoluted using three broad singlets, with the average positions at 221.0, 223.5, and 226.8 eV. We expected that two of them would be attributed to the main oxidation states of Nb found in the corresponding Nb 3d spectra (Nb⁰ and Nb⁵⁺), with their intensity ratio reflecting the intensity ratio of the Nb 3d doublets. However, this was not the case. The intensity ratio of the highest-BE peak relative to the sum of the lower-BE peaks appears smaller for the two low-Mo-content films (0.2) and rises for the higher-Mo-content films (0.55±0.1). This difference is, again, attributed to the background selection depending on the presence or absence of Mo 3d peaks.



Fig. S4. Experimental and curve-fitted narrow-scan (left column) combined Mo 3d and Nb 3d and (right column) individual Mo 3d XP spectra of the metallic precursor films and anodic films prepared in this study, focusing on the Nb 3d loss peaks and their deconvolution.

Further XPS figures and tables

Table S1. Summary of the binding energies (BEs), the full widths at half maxima (FWHMs), and the at.% of the components in the XP spectra in Fig. 4 of the main text. The BEs of the Mo $3d_{5/2}$ and Nb $3d_{5/2}$ peaks are listed.

PAA-free OX48-based films

	Mo 30	b		Nb 30	b		Al 2p		
OX48	state	BE/eV fwhm	at%	state	BE/eV fwhm	at%	state	BE/eV	fwhm at%
	Mo ⁶⁺ -OH	234.25 1.60	16	Nb ⁵⁺	207.10 1.10 7	'3.1	Al ³⁺	74.65	1.70 71.3
	Mo ⁶⁺	232.45 1.60	40	Nb ⁴⁺	205.55 1.20	2.0	Al ⁰	72.10	0.80 28.7
	Mo ⁵⁺	231.00 1.65	31	Nb ³⁺	203.85 1.40	2.0			
	Mo ⁴⁺	229.25 1.60	13	Nb ²⁺	202.30 1.10	3.3			
	Nb loss1	226.00 4.00	n/a	Nb ⁰	201.40 0.50 1	9.6			
	Nb loss2	222.50 3.80	n/a						
	Nb loss3	220.15 2.00	n/a						
OX48-220	state	BE/eV fwhm	at%	state	BE/eV fwhm	at%	state	BE/eV	fwhm at%
	Mo ⁶⁺ -OH	234.30 1.70	5	Nb ⁵⁺	207.30 1.15 9	95.9	Al ³⁺ -OH	76.15	1.60 9.4
	Mo ⁶⁺	232.35 1.45	13	Nb ⁴⁺	205.70 1.20	2.6	Al ³⁺	74.45	1.50 89.0
	Mo ⁵⁺	230.85 1.60	30	Nb ³⁺	204.40 1.20	0.6	Al ⁰	72.05	0.95 1.6
	Mo ⁴⁺	229.55 1.60	52	Nb ⁰	202.55 0.60	0.9			
	Nb loss1	227.00 4.00	n/a						
	Nb loss2	223.75 3.30	n/a						
	Nb loss3	221.25 2.70	n/a						
air appealed	stato	RE(a)/futher	ot ⁰ /	stata	RE/o)/fwbm		ototo		fubre at%
	Slale	DE/ev Iwnin	al 70	state		al 70	state	DE/ev	IWIIII al70
0/40-220	Mo ⁶⁺	232.50 1.55	31	Nb ⁵⁺ -OH	207.95 1.30	4.0	Al ³⁺ -OH	75.85	1.80 12.1
	M0 ⁵⁺	231.25 1.60	39	ND ⁵⁺	207.15 1.05 9	94.1	Al ³⁺	74.40	1.60 86.3
	MO ⁴⁺	229.85 1.60	30		205.70 1.30	1.3	Al	72.10	0.75 1.6
	ND IOSS1	227.00 4.00	n/a	IND ³⁺	204.40 1.30	0.6			
	ND IOSS2	223.65 3.00	n/a						
	IND IOSS3	221.20 2.80	n/a						
vacuum-annealed	state	BE/eV fwhm	at%	state	BE/eV fwhm	at%	state	BE/eV	fwhm at%
OX48-220	Mo ⁶⁺	232.65 1.50	61	Nb₅+-OH	208.00 1 20	7.4	Al3+-OH	76.10	1.70 13.4
	Mo ⁵⁺	231.25 1.50	26	Nb ⁵⁺	207.20 1.05 9)1.9	Al ³⁺	74.90	1.85 86.6
	Mo ⁴⁺	229.70 1.55	13	Nb ⁴⁺	205.50 1.20	0.7			
	Nb loss1	227.00 4.00	n/a						
	Nb loss2	223.55 3.65	n/a						
	Nb loss3	221.10 2.60	n/a						

The effect of re-anodizing voltage and Nb interlayer thickness



Fig. S5. Experimental and curve-fitted narrow-scan (left column) Mo 3d, (middle column) Nb 3d, and (right column) Al 2p XP spectra of the OX48-based films re-anodized to (a–c, g–i) 180 V or (d–f, j–l) 220 V, made from the (a–f) Al/25nmNb/Mo or (g–l) Al/15nmNb/Mo trilayer, to show the effect of the re-anodizing voltage and the Nb-interlayer thickness on the Mo content. The corresponding peak positions, FWHMs, and at.% of the components are summarized in Table S2.

Table S2. Summary of the BEs, FWHMs, and at.% of the components in the XP spectra shown in Fig. S5. The BEs of Mo $3d_{5/2}$ and Nb $3d_{5/2}$ peaks are listed.

The effect of re-anodizing voltage and Nb interlayer thickness

	Mo 3d	Nb 3d Al 2p					
OX48-180	state BE/eV fwhm	at% state BE/eV fwhm at%	<u>state</u> BE/eV fwhm at%				
	Mo ⁶⁺ -OH 234.30 1.70	9 Nb ⁵⁺ 207.25 1.15 95.	5 Al ³⁺ -OH 75.85 1.80 15.1				
	Mo ⁶⁺ 232.30 1.60	17 Nb ⁴⁺ 205.55 1.30 2.	1 <mark>Al³⁺ 74.35</mark> 1.50 82.9				
	Mo ⁵⁺ 230.75 1.70	29 Nb ^o 202.35 0.65 2.	4 Al ^o 72.10 0.95 2.0				
	Mo ⁴⁺ 229.50 1.70	45					
	Nb loss1 227.00 4.00	n/a					
	Nb loss2 223.60 3.75	n/a					
	Nb loss3 221.05 2.80	n/a					

OX48-220	state	BE/eV	fwhm	at%	state	BE/eV fwhm	at%	state	BE/eV	fwhm	at%
	Mo ⁶⁺ -Ol	H 234.30	1.70	5	Nb ⁵⁺	207.30 1.15	95.9	Al ³⁺ -OH	76.15	1.60	9.4
	Mo ⁶⁺	232.35	1.45	13	Nb ⁴⁺	205.70 1.20	2.6	Al ³⁺	74.45	1.50	89.0
	Mo ⁵⁺	230.85	1.60	30	Nb ³⁺	204.40 1.20	0.6	Alo	72.05	0.95	1.6
	Mo ⁴⁺	229.55	1.60	52	Nb ⁰	202.55 0.60	0.9				
	Nb loss	1 227.00	4.00	n/a							
	Nb loss	2 223.75	3.30	n/a							
	Nb loss	3 221.25	2.70	n/a							

OX48-180-15nmNb	state	BE/eV1	fwhm	at%	state	BE/eV1	fwhm	at%	state	BE/eV	fwhm	at%
	Mo ⁶⁺ -OH	234.15	1.70	6	Nb ⁵⁺	207.30	1.15	88.3	Al ³⁺ -OH	76.15	1.70	9.6
	Mo ⁶⁺	232.35	1.40	13	Nb ⁴⁺	205.60	1.20	3.4	Al ³⁺	74.45	1.55	85.2
	Mo ⁵⁺	231.05	1.50	26	Nb ³⁺	204.40	1.20	1.4	Al ^o	72.15	0.85	5.2
	Mo ⁴⁺	229.65	1.60	55	Nb ⁰	202.50	0.45	6.9				
	Nb loss1	227.00	4.00	n/a								
	Nb loss2	223.60	3.50	n/a								
	Nb loss3	221.10	2.65	n/a								

state	BE/eV f	whm	at%		state	E
Mo ⁶⁺ -OH	234.30	1.70	6		Nb ⁵⁺	2
Mo ⁶⁺	232.10	1.60	21		Nb4+	2
Mo ⁵⁺	230.75	1.60	34		Nb ³⁺	2
Mo ⁴⁺	229.60	1.60	39		Nb ⁰	2
Nb loss1	227.00	4.00	n/a			
Nb loss2	223.70	3.05	n/a			
Nb loss3	221.25	2.60	n/a			
	state Mo ⁶⁺ -OH Mo ⁶⁺ Mo ⁵⁺ Mo ⁴⁺ Nb loss1 Nb loss2 Nb loss3	state BE/eV f Mo ⁶⁺⁻ OH 234.30 Mo ⁶⁺ 232.10 Mo ⁵⁺ 230.75 Mo ⁴⁺ 229.60 Nb loss1 227.00 Nb loss2 223.70 Nb loss3 221.25	state BE/eV fwhm Mo ⁶⁺⁻ OH 234.30 1.70 Mo ⁶⁺ 232.10 1.60 Mo ⁵⁺ 230.75 1.60 Mo ⁴⁺ 229.60 1.60 Nb loss1 227.00 4.00 Nb loss2 223.70 3.05 Nb loss3 221.25 2.60	state BE/eV fwhm at% Mo ⁶⁺⁻ OH 234.30 1.70 6 Mo ⁶⁺ 232.10 1.60 21 Mo ⁵⁺ 230.75 1.60 34 Mo ⁴⁺ 229.60 1.60 39 Nb loss1 227.00 4.00 n/a Nb loss2 223.70 3.05 n/a Nb loss3 221.25 2.60 n/a	state BE/eV fwhm at% Mo ⁶⁺ -OH 234.30 1.70 6 Mo ⁶⁺ 232.10 1.60 21 Mo ⁵⁺ 230.75 1.60 34 Mo ⁴⁺ 229.60 1.60 39 Nb loss1 227.00 4.00 n/a Nb loss2 223.70 3.05 n/a	state BE/eV fwhm at% state Mo ⁶⁺⁻ OH 234.30 1.70 6 Nb ⁵⁺ Mo ⁶⁺ 232.10 1.60 21 Nb ⁴⁺ Mo ⁵⁺ 230.75 1.60 34 Nb ³⁺ Mo ⁴⁺ 229.60 1.60 39 Nb ⁰ Nb loss1 227.00 4.00 n/a Nb loss2 223.70 3.05 n/a Nb loss3 221.25 2.60 n/a

state	BE/eV f	whm	at%	state	BE/eV	fwhm	at%
Nb ⁵⁺	207.20	1.15	97.5	Al ³⁺ -OH	76.00	1.75	15.0
Nb ⁴⁺	205.55	1.20	1.5	Al ³⁺	74.30	1.45	84.1
Nb ³⁺	204.20	1.30	0.6	Alo	72.00	0.70	0.9
Nb ⁰	202.25	0.60	0.4				

PAA-half-etched and PAA-free OX48-220-based films



Fig. S6. Experimental and curve-fitted narrow-scan (left column) Mo 3d, (middle column) Nb 3d, and (right column) Al 2p XP spectra of PAA-half-etched OX48-220-based anodic films (made from the Al/25nmNb/Mo trilayer): (a–c) the as-prepared OX48-220 and (g–i) air-annealed OX48-220 films. The corresponding PAA-free films are shown here again for comparison (d–f, j–l). The corresponding peak positions, FWHMs, and at.% of the components are summarized in Table S3.

Table S3. Summary of BEs, FWHMs, and at.% of the components in the XP spectra in Fig. S6. The BEs of Mo $3d_{5/2}$ and Nb $3d_{5/2}$ peaks are listed.

	Mo 3d		Nb 3	d	Al 2p		
as-prepared	state	BE/eV fwhm at%	state	BE/eV fwhm at%	state	BE/eV f	whm at%
PAA-half-etched	Mo ⁶⁺ -OF	233.90 1.70 8	Nb ⁵⁺	207.00 1.45 100	Al ³⁺	74.80	1.70 100
	Mo ⁶⁺	232.30 1.50 33					
	Mo ⁵⁺	231.00 1.55 32					
	Mo ⁴⁺	229.75 1.65 27					
	Nb loss?	1 227.00 4.00 n/a					
	Nb loss2	2 223.70 3.15 n/a					
	Nb loss	3 221.20 2.80 n/a					
as-prepared	state	BE/eV fwhm at%	state	BE/eV fwhm at%	state	BE/eV f	whm at%
PAA-free	Mo ⁶⁺ -OF	234.30 1.70 5	Nb ⁵⁺	207.30 1.15 95.9	Al ³⁺ -OH	76.15	1.60 9.4
OX48-220 film	Mo ⁶⁺	232.35 1.45 13	Nb ⁴⁺	205.70 1.20 2.6	Al ³⁺	74 45	1.50.89.0
	Mo ⁵⁺	230.85 1.60 30	Nb ³⁺	204.40 1.20 0.6		72.05	0.95 1.6
	Mo ⁴⁺	229.55 1.60 52	Nb ⁰	202.55 0.60 0.9			0100 110
	Nb loss'	1 227.00 4.00 n/a					
	Nb loss2	2 223.75 3.30 n/a					
	Nb loss3	3 221.25 2.70 n/a					
air-annealed	state	BE/eV fwhm at%	state	BE/eV fwhm at%	state	BE/eV f	whm at%
PAA-half-etched	Mo ⁶⁺	232.40 1.60 53	Nb ⁵⁺ -Ol	H 207.95 1.20 6.1	Al ³⁺	74.90	1.80 100
OX48-220 film	Mo ⁵⁺	230.80 1.60 33	Nb ⁵⁺	207.05 1.10 93.9			
	Mo ⁴⁺	229.50 1.60 14					
	Nb loss'	1 227.00 4.00 n/a					
	Nb loss2	2 223.40 3.40 n/a					
pttt	Nb loss3	3 221.10 2.50 n/a					
air-annealed	state	BE/eV fwhm at%	state	BE/eV fwhm at%	state	BE/eV f	whm at%
PAA-free	Mo ⁶⁺	232.50 1.55 31	Nb ⁵⁺ -Ol	H 207.95 1.30 4.0	Al ³⁺ -OH	75.85	1.80 12.1
OX48-220 film	Mo ⁵⁺	231.25 1.60 39	Nb ⁵⁺	207.15 1.05 94.1	Al ³⁺	74.40	1.60 86.3
	Mo ⁴⁺	229.85 1.60 30	Nb ⁴⁺	205.70 1.30 1.3	Al ^o	72.10	0.75 1.6
	Nb loss?	1 227.00 4.00 n/a	Nb ³⁺	204.40 1.30 0.6			
	Nb loss2	2 223.65 3.00 n/a					
	Nb loss	3 221.20 2.80 n/a					

PAA-half-etched and PAA-free OX48-220-based films

XRD interpretation



Fig. S7. 2D and extracted conventional as-recorded, calculated, and difference diffractograms of the OX48-based samples: as-prepared OX48, OX48-180, and OX48-220 samples, vacuum-annealed OX48-220 and air-annealed OX48-220. Sample codes are explained in Fig. 1 and Fig. 2 of the main text.

XRD examination: The main refinement parameters and quantitative phase analysis

The Rietveld refinement (Rietveld, 1969) was performed with the TOPAS v6 software (Bruker AXS GmbH, 2017; Coelho, 2018). The background was modeled with a 2nd-order Chebyschev polynomial. The instrumental contribution to the diffraction profile was calculated with the LaB₆ (NIST SRM 660c). The relative quantitative phase analysis was obtained by refining the Rietveld scale factor for each phase and applying the corresponding well-known equations (Hill & Howard, 1987). The peak width of each phase was modeled with the Double-Voigt Approach (Balzar, 1999) by considering the Lorentzian contribution (for minor phases) and also the Gaussian contribution (for major phases) of the crystallite size effect and discarding any contribution of the microstrain to the peak width. The averaged integral breadth was obtained from the resulting fitted Voigt function to the whole diffractogram. The Scherrer equation (Stokes & Wilson, 1942) was then applied to obtain the apparent crystallite size. The preferred orientation effect was corrected with the March-Dollase model (Dollase, 1986; March, 1932). The error in wt.% estimated for minor phases is higher due to the high preferred orientation. The refinement process results in a high correlation between the Rietveld scale factor, which is directly related to wt.%, and the March-Dollase parameter, which corrects the preferred orientation.

Balzar, D. (1999). Voigt-function model in diffraction line-broadening analysis. In R. L. Snyder, J. Fiala, & H. J. Bunge (Eds.), *Defect and Microstructure Analysis by Diffraction (International Union of Crystallography Monographs on Crystal)* (pp. 94–124). Oxford University Press. https://doi.org/10.1.1.30.7311

Bruker AXS GmbH. (2017). TOPAS 6 Technical Reference.

Coelho, A. A. (2018). TOPAS and TOPAS-Academic: An optimization program integrating computer algebra and crystallographic objects written in C++. *Journal of Applied Crystallography*, *51*, 1–9. https://doi.org/10.1107/S1600576718000183

Dollase, W. A. (1986). Correction of Intensities of Preferred Orientation in Powder Diffractometry: Application of the March Model. *Journal of Applied Crystallography*, *19*(pt 4), 267–272. https://doi.org/10.1107/S0021889886089458

Hill, R. J., & Howard, C. J. (1987). Quantitative phase analysis from neutron powder diffraction data using the Rietveld method. *Journal of Applied Crystallography*, 20(6), 467–474. https://doi.org/10.1107/S0021889887086199

March, A. (1932). Mathematische Theorie der Regelung nach der Korngestah bei affiner Deformation. Zeitschrift Für Kristallographie - Crystalline Materials, 81(1), 285–297. https://doi.org/10.1524/zkri.1932.81.1.285

Rietveld, H. M. (1969). A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography*, 2(2), 65–71. https://doi.org/10.1107/S0021889869006558

Stokes, A. R., & Wilson, A. J. C. (1942). A method of calculating the integral breadths of Debye-Scherrer lines. *Mathematical Proceedings of the Cambridge Philosophical Society*. https://doi.org/10.1017/S0305004100021988

Table S4. The main refinement parameter and results of quantitative phase analysis performed for all OX48-based samples prepared in this work.

Sample	OX48			
File	TI05810002	Rwp		6.70
Phase	S.G. / Cell (Å)	Cryst. Size (nm)	РО	wt.%
Мо	Im3m 3.15425(6)	20.4(2)	<110> 0.380(2)	96(3)
Nb	Im3m 3.3228(3)	12.2(3)	<110> 0.26(5)	4(3)
				·
Sample	OX48-180			
File	T102320098	Rwp	DO	7.87
Phase	S.G. / Cell (A)	(nm)	PO	wt.%
Мо	Im3m 3.15276(7)	20.1(3)	<110> 0.402(3)	98(2)
Nb	Im3m 3.351(3)	4.8(6)	<110> 0.3(3)	2(2)
Samela	OV40 220			
Sample Filo	UA48-220 TI05810007	Dum	<u> </u>	6.80
Phase	S.G. / Cell (Å)	Cryst. Size	РО	wt.%
Мо	Im3m 3.15665(7)	20.2(3)	<110> 0.390(3)	100
Samula	OV 19 220 years	um annealed		
Sample Filo	TI02220088	Dum		8 27
Phase Phase	S.G. / Cell (Å)	Cryst Size	PO	0.57
Thase	5.0.7 CCII (A)	(nm)	10	Wt. 70
Мо	Im3m 3.14574(7)	28.2(5)	<110> 0.355(3)	74(10)
MoO ₂	P2 ₁ /c 5.614(5) 4.833(4) 5.608(3) 120.81(5)	19(2) §	<212> 0.57(3)	24(8)
Nb ₂ O ₅	Pbam 6.205(8) 29.1(3) 3.90(5)	19(4) §	<001> 1.3(3) <100> 0.20(17)	1.6(19)
0 1	ON/40 000 ·			
Sample File	UX48-220 air-ai	nnealed	I	<u> </u>
Phase	S.G. / Cell (Å)	Cryst. Size	РО	wt.%
Мо	$Im\bar{3}m$ 3 14786(8)	23.8(4)	<110> 0.397(3)	63(13)
MoO ₂	$\begin{array}{c} P2_{1}/c \\ 5.624(3) \\ 4.841(3) \\ 5.633(2) \\ 120.95(3) \end{array}$	19.5(11)	<212> 0.66(2)	33(12)
Nb ₂ O ₅	Pbam 6.215(3) 29.1(2) 3.9123(5)	27.7(13)	<001> 0.39(4) <100> 0.1(9)	5(3)
§ The Crystallite Si	ize for these phases has b	een fixed because of t	the low-intensity pea	aks

Justification of the crystalline-oxide location in the annealed samples

This calculation aimed to confirm where the crystalline oxides reside in the air- and vacuumannealed OX48-220 samples (Fig. 7, Fig. S7) - in the bottom-oxide layer or/and in the rods' cores. We estimated the wt.% of the phases from the geometrical parameters of the films revealed by the SEM analysis, considering the thickness of the remaining Mo layer (SEM-based wt.%), and compared them with the wt.% obtained by the XRD analysis. The assumption about the location of crystal phases preferentially in the bottom oxide was based on our previous experience with various PAA-assisted re-anodized and annealed nanostructured anodic oxides.^{1,2,3,4}

Fig. S8 shows schematics of the as-prepared OX48-220 film, indicating the thicknesses of metallic Mo remaining below the anodic film after completing the anodizing and re-anodizing processes, the thickness of MoO_2 in the bottom oxide, and the thickness of NbO_x in the bottom oxide. The thicknesses remain unchanged after the annealing procedures, which is concluded based on the SEM cross-sectional analysis of the annealed films and monitoring the intensity of (110) Mo peak (Fig. S7).

From the geometrical parameters (Fig. S8), we calculated the vol.% of the materials (see Table S5). For example, the vol.% of Mo was 130/(130+95+25) = 52 vol.%. Based on the material densities, the SEM-based vol.% were recalculated into the SEM-based wt.%, and these were compared with the XRD-based wt.% for the two samples. All the values are listed in Table S5. As one may see, the XRD-based wt.% of the oxide phases in the two films are nearly the same or lower than the SEM-based wt.%. Therefore, the two oxide phases in the two samples reside merely within the bottom-oxide layer (bottom-oxide nanoballs).

Fig. S8. Schematics of the OX48-220 film used for calculating SEM-based wt.% of crystal phases (if they would fill the whole bottom-oxide layer), to be compared with the XRD analysis results (Fig. 7, Fig. S7, and Table 4).

Material	Density $(g \text{ cm}^{-3})$	SEM-based thickness (nm)	SEM-based vol. fraction	SEM-based wt. fraction	Air-annealed film: XRD-based wt.	Vacuum-annealed film: XRD-based wt. fraction
Ma	10.22	120	(V01.%)	(WL.%)	fraction (wt.%)	(wt.%)
MoO ₂	6.47	95	32 38	04 30	03(13) 33(12)	74(10)
Nb ₂ O ₅	4.60	25	10	6	5(3)	1.6(19)

Table S5. A summary of material parameters and various fractions of crystalline materials used for evaluating the location of the crystalline oxide phases in the annealed OX48-220 samples.

Quantitative analysis of the film formation mechanism

In the following calculation, we will estimate whether the amount of the various oxides generated during the formation of the OX48-180 sample is sufficient to form the individual parts of the nanostructured film, i.e., the bottom oxide, the rods' shells, and the rods' cores.

The starting data for this calculation was the thicknesses of the Nb and Mo layers consumed during the anodizing/re-anodizing. The thickness of consumed Nb is equal to its initial thickness (25 ± 5 nm). The thickness of the consumed Mo was estimated to be 25 ± 5 nm, which is the difference between the initial (170 nm) and remaining after the re-anodizing (145 nm) thicknesses of the Mo layer. The initial and remaining thicknesses of the Mo layer were obtained from numerous SEM images of the sample cross sections (as in Fig. S2 and Fig. S3); the wavy (concave) profile of the Mo/MoO_x interface after the anodizing/re-anodizing (Fig. 2, Fig. 9) was also taken into account.

The following equivalent compact anodic films would grow from a 25 nm thick Nb and a 25 nm thick Mo: 63 nm of Nb₂O₅ and 67.5 nm of MoO_{2.5}, assuming the Pilling-Bedworth ratios, PBR, of 2.5 and 2.7, respectively. An average composition of the MoO_x oxide with x = 2.5 was selected to account for the mixed valency of MoO_x revealed by the XPS analysis. The PBR of MoO_{2.5} was selected as an average value for MoO₃ (3.27) and MoO₂ (2.11), which were calculated from the densities and molar masses of the various materials, as listed in Table S6.

Table S6. A summary of parameters of the metals and oxides used for calculating oxide Pilling-Bedworth ratios (PBR).

Material	Density	Molar mass	PBR: calculated	PBR: from literature
	$(g \text{ cm}^{-3})$	$(g \text{ mol}^{-1})$		
Nb	8.582	92.906	_	_
Nb_2O_5	4.60	265.81	2.67	2.5 [5]
Mo	10.223	95.95	-	_
MoO ₃	4.69	143.95	3.27	3.26 [5]
MoO ₂	6.47	127.94	2.11	_
MoO _{2.5}	_	-	2.69	_

Fig. S9 depicts the top view of the OX48-180 film inherited from Fig. 9f, indicating the area used for the calculation, confined within the red triangle. One-half of a nanorod and one-half of a bottom-oxide ball are involved in the triangle, with its area $S_{\Delta} = D_{\text{cent}}a/2 = 6235 \text{ nm}^2$, where D_{cent} is the center-to-center distance (120 nm) and $a = \sqrt{(3/2)} D_{\text{cent}}$.

The volumes of the oxides grown within the triangle are

 $V_{\text{Nb2O5}} = dS_{\Delta} = 63 \text{ nm} \times 6235 \text{ nm}^2 = 3.93 \times 10^5 \text{ nm}^3 \text{ and } V_{\text{MoO2.5}} = 67.5 \text{ nm} \times 6235 \text{ nm}^2 = 4.21 \times 10^5 \text{ nm}^3$,

which are the oxides available to form the bottom-oxide balls, nanorods' cores, and shells within the triangle (the colors correspond to the two oxides). The total available oxide volume is thus $\sim 8.14 \times 10^5$ nm³. The error of calculating these volumes is relatively high because the accuracy of estimating the metal-film thicknesses by SEM is about ±5 nm; therefore, the volume-estimation error may reach ~20% for each oxide.

Fig. S9. Schematic surface image to estimate the geometrical parameters of the OX48-180 film used for calculating the amount of the various oxides in the nanostructured film. The calculation was done within the area marked by the red triangle, involving $\frac{1}{2}$ of a nanorod and $\frac{1}{2}$ of a bottom-oxide ball. The schematic is inherited from Fig. 9f.

Further, we calculated the approximate volumes of oxide material needed for forming the various parts of the OX48-180 film. A bottom-oxide ball was approximated with a pressed ball, i.e., a spheroid, having two axes of D_{cent} and one of d_{BO} (bottom-oxide thickness $d_{BO} = 102$ nm). Thus, its volume within the red triangle is

$$V_{\rm BO} = 1/2 \times 4/3\pi \left(D_{\rm cent}/2\right)^2 (d_{\rm BO}/2) = 1/12 \times \pi \times 120^2 \times 102 = 3.84 \times 10^5 \text{ nm}^3.$$

This value is likely underestimated since the balls are even more pressed along the substrate, so the real $V_{\rm BO}$ value lies somewhere between 3.84×10^5 nm³ and the volume of an entirely uniform compact bottom oxide $V_{\rm BO,max} = 102$ nm $\times 6235$ nm² = 6.36×10^5 nm³, which is around 4.7×10^5

nm³. About one-third of this volume $(1.57 \times 10^5 \text{ nm}^3)$ should belong to Nb₂O₅, whereas the rest belongs to MoO₂ $(3.13 \times 10^5 \text{ nm}^3)$.

The neck of a rod (its diameter is equal to the pore diameter $d_p = 29$ nm, and its height is about 45 nm, leading to a volume of half of the neck of 1.5×10^4 nm³) has a small volume and probably quite a mixed composition, so its contribution was neglected.

From the rod's core diameter $d_p = 29$ nm and its height $h_{rod} = 405$ nm - 45 nm = 360 nm, the core's volume within the red triangle is

 $V_{\text{core}} = 1/2 \times \pi (d_p/2)^2 h_{\text{rod}} = 1.19 \times 10^5 \text{ nm}^3.$

The cores are assumed to be pure MoO_x , alumina- and niobia-free. Giving the nanorods' shells have the inner diameter $d_p = 29$ nm, the outer diameter $d_{rod} = 50$ nm, and the height $h_{rod} = 405$ nm – 45 nm = 360 nm, the shells' volume within the red triangle is

$$V_{\text{shell}} = 1/2 \times \pi \left[(d_{\text{rod}}/2)^2 - (d_p/2)^2 \right] h_{\text{rod}} = 2.34 \times 10^5 \text{ nm}^3.$$

The shell material contains about 50 at.% Al, 40 at.% Nb, and 10 at.% Mo, which is recalculated into 31.3 vol.% Al₂O₃, 56.8 vol.% Nb₂O₅, and 11.9 vol.% MoO_{2.5}, resulting in 1.61×10^5 nm³ in total for the two oxides (2.8×10^4 nm³ of MoO_x + 1.33×10^5 nm³ of Nb₂O₅).

The obtained volumes are summarized in Table S7. Comparing the total available and needed volumes for each oxide, one may see that they agree pretty well (within the estimated error), which means that the various places in the nanostructured film were formed in the way suggested in Fig. 6 and 9, i.e., having the cores of MoO_x , free from alumina and niobia. An indirect support for such a distribution is the electrochemical behavior, which will be described later in the text. From comparing the available and needed volumes, it may be concluded that the film-growth model sketched in Fig. 9 is accurate.

Table S7. A summary of the oxide volumes calculated for the OX48-180 sample within the red triangle in Fig. S9.

		Nb ₂ O ₅	MoO _x
Total available volume (nm ³)	3.93 × 10 ⁵ (20%)	$4.21 \times 10^5 (20\%)$
	bottom oxide	$1.57 \times 10^5 (30\%)$	$3.13 \times 10^5 (30\%)$
Needed volume to fill the	rods' core	-	$1.19 \times 10^5 (10\%)$
various film parts (nm ³)	rods' shell	$1.33 \times 10^5 (10\%)$	$2.8 \times 10^4 (10\%)$
	total	$2.9 \times 10^5 (30\%)$	4.6 × 10⁵ (30%)

Electrochemical analysis - additional data and interpretations

Additional notes to the experimental part: Galvanostatic charge-discharge (GCD) measurements were performed in the borate buffer by applying a constant negative current for 60 s to charge the electrode, and the potential was recorded.

The EIS was carried out in the borate buffer by applying a sinusoidal perturbation of 10 mV to the open-circuit potential (OCP) or selected bias voltages (for Mott-Schottky measurements) in a frequency range of 1.0 MHz to 0.01 or 0.1 Hz. For Mott-Schottky evaluation, each EIS measurement lasted 3 min. The experimental EIS data were analyzed using computer simulation and fitting software Autolab NOVA (version 1.10). The entire frequency range was used for fitting with an equivalent electrical circuit containing a constant phase element (CPE) in parallel with a resistor, from which the capacitances were extracted $C = Y_0^{1/n} R_p^{(1-n)/n}$, although only for the electrochemical double layer.

Fig. S10. Examination of the available potential window. Cyclic voltammetry (CV) curves obtained for the as-prepared PAA-inbuilt OX48-180 film in the borate buffer with a scan rate of 50 mV s⁻¹: extending the (a) negative and (b) positive range to find the onsets of H₂ and O₂ evolution, respectively.

Fig. S11. The calculation of charge (q) from the CV in Fig. 10a as $q = \int i(t) dt$, which is equal to the capacity. For example, the charge of 0.35 mC during the charging is equal to a capacity of 0.41 µAh cm⁻².

Fig. S12. Galvanostatic charge-discharge (GCD) curves obtained for the as-prepared PAA-inbuilt OX48-180 film in the borate buffer at various current densities for 60 s (the negative current leads to charging of the electrode material): (a,b) potential vs. time and (c,d) recalculated potential vs. capacity. Panels (b) and (d) show the corresponding zoomed-in parts. The quantities were calculated relative to the effective surface areas (A_e). The capacity shown in Fig. 10b was calculated by integrating the area above the green curve in the whole measured potential range (the calculation was performed according to Ref. 7 using Eq. 140 and Fig. 42c for the negative electrodes, also according to Ref. 8 using Eq. 1).

Mott-Schottky analysis

For the as-prepared PAA-inbuilt OX48-180 film, we measured a series of EIS spectra at potentials ranging from -0.1 to -1.9 V vs. Ag/AgCl in 0.2V steps (Fig. S13a,b), to perform Mott-Schottky analysis^{9,10,11,12,13} and estimate the donor concentration in the MoO₃ at the rod tops, which was supposed to be an *n*-type semiconductor.¹⁴ However, for battery-like and pseudocapacitive materials, various contributions to the total impedance were expected besides the capacitance of the depletion layer;¹⁵ therefore, an evaluation using a physically meaningful electrical equivalent circuit was needed. The acquired data (Fig. S13a,b) indicated the presence of two time constants. Therefore, we used the circuit shown in the inset of Fig. S13b, which consists of a series resistance (R_s) and two R_p -CPE pairs connected in series, whereas the one having a higher R_p value (i.e., $R_{p,1}$) also contained Warburg impedance (which is a CPE with n = 0.5, labeled as CPE_w, its necessity is shown in Fig. S14). The agreement between the experimental and fitted EIS data (Fig. S13a,b) indicate that the circuit suits the measured dataset. Based on the literature^{7,8,15} and our previous experience,^{10,11} we assign the CPE₂ and $R_{p,2}$ to an electrical double layer, the CPE₁ and $R_{p,1}$ to either a depletion layer or pseudocapacitance, depending on whether the potential is above or below the flat-band potential (which is around -1.2 V vs. Ag/AgCl, Fig. S13c), respectively, and the CPE_W to diffusion impedance originating from ion migration in the film and/or related to H₂ evolution.

The calculated capacitance of the electrical double layer, when related to $A_{\rm e}$, is 30–70 µF cm⁻², which is slightly higher than that expected for an electrical double layer (10–40 µF cm⁻²).¹⁶ The corresponding parallel resistance ($R_{\rm p,2}$) is very low (5–10 Ω cm², related to $A_{\rm e}$). Such values reinforce our assignment of CPE₂ and $R_{\rm p,2}$ to an electrical double layer.

The admittance, Y_0 , value of CPE₁ increases with decreasing applied potential (Fig. S13c, left yaxis, related to A_e), indicating a transition from a depletion layer on the MoO₃ rod tops to a conducting oxide around -1.0 V vs. Ag/AgCl. If the capacitances are calculated using C = Y01/n Rp(1-n)/n,6 which may be an incorrect approach due to Warburg impedance, they increase from ~120 to ~400 μ F cm⁻². The very high capacitances of the depletion layer (~120 μ F cm⁻²) and the relatively low *n*-values of CPE_1 (inset in Fig. S13c) indicate that the material is a highly doped semiconductor with an extremely thin depletion layer (~0.3 nm, assuming the dielectric constant, ε_r , of 35^{17}). When attempting to apply the Mott-Schottky equation^{10,11} to the slope obtained from the Mott-Schottky plot (Fig. S13c, right y-axis) to calculate an approximate donor concentration, N_d , we should have in mind that if the oxide turns into a conducting one at lower potentials, there would be an additional capacitive contribution to CPE_1 originating from the pseudocapacitance, which decreases the capacitance (or Y_0) and increases $1/Y_0^2$ in the Mott-Schottky plot in comparison with a semiconductor without an additional pseudocapacitive behavior. The slope in the Mott-Schottky plot is, therefore, ~2-fold lower than it would be if the semiconductor would not show pseudocapacitance, and the estimated N_d of 2×10^{22} cm⁻³ is, therefore, ~2-fold higher than in reality for the MoO₃ oxide present at the rod's tops.

In conclusion, the value for N_d estimated from the Mott-Schottky plot is ~1 × 10²² cm⁻³, corresponding to a highly doped *n*-type semiconductor.¹¹

Furthermore, the applied potential also influences the values for $R_{p,1}$ and CPE_W (Fig. S13d, related to A_e , while $R_{p,1}$ is the charge-transfer resistance of the depletion layer): $R_{p,1}$ decreases 20-fold with decreasing potential, which can be expected. If the depletion layer disappears, the oxide becomes fully conducting, and the $Y_{0,W}$ increases substantially with decreasing potential, in agreement with the deconvoluted diffusive currents (Fig. 11e).

Baes on the above consideration and calculations, one may see that the results of Mott-Schottky measurements (Fig. S13c,d) agree with the deconvolution of the CV currents, showing a transition from a depletion layer to a conducting oxide in the cathodic scan direction, enabling Na⁺ intercalation.

Fig. S13. EIS measurements combined with Mott-Schottky analysis for the as-prepared PAA-inbuilt OX48-180 film. (a,b) Experimental (symbols) and fitted (solid lines) Bode plots at potentials ranging from -0.1 to -1.9 V vs. Ag/AgCl in 0.2V steps (selected EIS data are shown, V stands in the legends for V vs. Ag/AgCl). The inset in (b) describes the electrical equivalent circuit used for fitting. (c,d) Parameters of CPE₁, $R_{p,1}$, and CPE_w vs. applied potential obtained by fitting the EIS curves in (a,b): (c) admittance (Y_0), $1/Y_0^2$, and *n*-value of CPE₁, (d) $R_{p,1}$ and $Y_{0,w}$ of CPE_w. The impedance in (a) is related to A_a , whereas the values in (c) and (d) are related to A_e .

Fig. S14. The need to consider Warburg impedance in the selected electrical equivalent circuit is manifested for the two EIS measurements performed on the as-prepared PAA-inbuilt OX48-180 film (shown in Fig. S13a,b) obtained at -0.5 and -1.1 V vs. Ag/AgCl. The upper graphs show the Bode plots; the lower graphs show the corresponding Nyquist plots. The symbols are the experimental points, the lines are the fits, and the blue or red lines represent the fit with or without the Warburg impedance, respectively. The difference between the two fitting approaches is significant in the low-frequency range.

References

- 1 A. Mozalev, M. Bendova, F. Gispert-Guirado, E. Llobet, Hafnium-oxide 3-D nanofilms via the anodizing of Al/Hf metal layers, Chem. Mater. 30 (2018) 2694–2708. <u>http://dx.doi.org/10.1021/acs.chemmater.8b00188</u>.
- M. Bendova, J. Kolar, M. Marik, T. Lednicky, A. Mozalev, Influence of nitrogen species on the porous-aluminaassisted growth of TiO₂ nanocolumn arrays, Electrochim. Acta 281 (2018) 796–809. <u>https://doi.org/10.1016/j.electacta.2018.05.197</u>.
- 3 M. Bendova, J. Kolar, F. Gispert-Guirado, A. Mozalev, Porous-alumina-assisted growth of nanostructured anodic films on Ti–Nb alloys, ChemElectroChem 5 (2018) 2825–2835. <u>https://doi.org/10.1002/celc.201800785</u>.
- 4 K. Kamnev, M. Sepúlveda, M. Bendova, Z. Pytlicek, J. Prasek, E. Kolibalova, J. Michalicka, A. Mozalev, 2021. The growth, composition, and functional properties of self-organized nanostructured ZrO₂-Al₂O₃ anodic films for advanced dielectric applications. Adv. Electron. Mater. 7, 2100505. <u>https://doi.org/10.1002/aelm.202100505</u>.
- 5 J.P.S. Pringle, The anodic oxidation of superimposed metallic layers: theory, Electrochim. Acta, 25 (1980) 1423– 1437. <u>https://doi.org/10.1016/0013-4686(80)87157-X</u>.
- 6 B. Hirschorn, M.E. Orazem, B. Tribollet, V. Vivier, I. Frateur, M. Musiani, Determination of effective capacitance and film thickness from constant-phase element parameters, Electrochim. Acta 55 (2010) 6218–6227. https://doi.org/10.1016/j.electacta.2009.10.065.
- 7 A. Noori, M.F. El-Kady, M.S. Rahmanifar, R.B. Kaner, M.F. Mousavi, Towards establishing standard performance metrics for batteries, supercapacitors and beyond, Chem. Soc. Rev. 48 (2019) 1272–1341. <u>https://doi.org/10.1039/C8CS00581H</u>.
- 8 A.E. Elkholy, T.T. Duignan, X. Sun, X. Song Zhao, Stable α-MoO₃ electrode with a widened electrochemical potential window for aqueous electrochemical capacitors, ACS Appl. Energy Mater. 4 (2021) 3210–3220. https://doi.org/10.1021/acsaem.0c02990.
- 9 A.J. Bard, LR. Faulkner, Electrochemical methods: Fundamentals and applications, second ed., John Wiley & Sons, Inc., New York, 2001.
- 10 A. Mozalev, M. Bendova, F. Gispert-Guirado, Z. Pytlicek, E. Llobet, Metal-substrate-supported tungsten-oxide nanoarrays via porous-alumina-assisted anodization: from nanocolumns to nanocapsules and nanotubes, J. Mater. Chem. A 4 (2016) 8219–8232. <u>https://doi.org/10.1039/C6TA02027E</u>.
- 11 M. Bendova, F. Gispert-Guirado, A.W. Hassel, E. Llobet, A. Mozalev, Solar water splitting on porous-aluminaassisted TiO₂-doped WO_x nanorod photoanodes: Paradoxes and challenges, Nano Energy 33 (2017) 72–87. <u>http://dx.doi.org/10.1016/j.nanoen.2017.01.029</u>.
- M. Bendova, Z. Pytlicek, J. Prasek, A. Mozalev, 2019. The growth and unique electronic properties of the porousalumina-assisted hafnium-oxide nanostructured films. Electrochim. Acta 327, 135029. <u>https://doi.org/10.1016/j.electacta.2019.135029</u>.
- 13 A. Mozalev, M. Bendova, F. Gispert-Guirado, E. Llobet, H. Habazaki, 2024. Porous-anodic-alumina-templated Ta-Nb-alloy/oxide coatings via the magnetron-sputtering/anodizing as novel 3D nanostructured electrodes for energy-storage applications, Surf. Coat. Technol. 489, 131042. <u>https://doi.org/10.1016/j.surfcoat.2024.131042</u>.
- 14 C.V. Ramana, A. Mauger, C.M. Julien, 2021. Growth, characterization and performance of bulk and nanoengineered molybdenum oxides for electrochemical energy storage and conversion, Prog. Cryst. Growth Charact. Mater. 67, 100533. <u>https://doi.org/10.1016/j.pcrysgrow.2021.100533</u>.
- 15 A. Adan-Mas, T.M. Silva, L. Guerlou-Demourgues, M. Fatima Montemor, Application of the Mott-Schottky model to select potentials for EIS studies on electrodes for electrochemical charge storage, Electrochim. Acta 289 (2018) 47–55. <u>https://doi.org/10.1016/j.electacta.2018.08.077</u>.
- 16 S. Fleischmann, J.B. Mitchell, R. Wang, C. Zhang, D. Jiang, V. Presser, V. Augustyn, Pseudocapacitance: From fundamental understanding to high power energy storage materials, Chem. Rev. 120 (2020) 6738–6782. <u>https://dx.doi.org/10.1021/acs.chemrev.0c00170</u>.
- B.A. Holler, K. Crowley, M.-H. Berger, X.P.A.Gao, 2020. 2D semiconductor transistors with van der Waals oxide MoO₃ as integrated high-κ gate dielectric, Adv. Electron. Mater. 6, 2000635. https://doi.org/10.1002/aelm.202000635.