

Supplementary Material

Table S1. Summary of RuO₂ based pH electrode characteristics reported previously and in this work

Deposition method	Electrode sensitive material	Substrate	Precursor	Slope, mV/pH	E ⁰ , mV	R ²	pH range	Response time, s	T, °C	Hysteresis, mV	Drift, mV/h	Reference electrode	Ref.
ED ¹	RuO ₂	Au wire	K ₂ RuO ₄	59.3	521	N/A	2.0 - 12.0	N/A	N/A	N/A	N/A	NHE ²	[1]
		Au disk	RuCl ₃ ·xH ₂ O	60.5	N/A	0.999	2.0 – 11.0	7	N/A	N/A	N/A		[2]
		Pt	RuO ₂	56.2	596	0.999	4.0 - 10.0	N/A	37.5	N/A	N/A	Ag AgCl KCl	[3]
		Pt-Ti	RuO ₂	59.3	609	0.999	4.0 - 10.0	N/A	37.5	N/A	N/A		[3]
Screen-printing	RuO ₂	Polyester foil	RuO ₂ -graphite	51.2	606	N/A	2.0 – 10.0	N/A	N/A	N/A	N/A	SCE ³	[4]
		Al ₂ O ₃	RuO ₂	58.4	578	0.995	2.0 – 12.0	14	22	N/A	0.5		[5]
		Al ₂ O ₃	RuO ₂ ·xH ₂ O	52.1	651	N/A	2.0 – 10.0	15	21 – 24	N/A	N/A	Ag AgCl KCl	[6]
		Al₂O₃	RuO₂	61.8	682	0.996	1.0 – 13.0	14	22	4.6 – 24.9	0.15		This study
	RuO ₂ -Ta ₂ O ₅	Al ₂ O ₃	RuO ₂ -glass ⁴	56.0	N/A	N/A	2.0 – 12.0	120	N/A	N/A	N/A	Screen printed Ag/AgCl	[7]
		Al ₂ O ₃	RuO ₂ , Ta ₂ O ₅ , glass powder	68.2	N/A	0.987	2.0 – 12.0	15	N/A	10	N/A	Screen printed Ag/AgCl	[7]
		Al ₂ O ₃	RuO ₂ , Ta ₂ O ₅	56	N/A	N/A	2.0 – 12.0	15	N/A	N/A	N/A		[8]
		Al ₂ O ₃	RuO ₂ , SnO ₂	56.5	631	0.998	2.0 – 12.0	9	N/A	7	N/A		[9]
		Al ₂ O ₃	RuO ₂ , Cu ₂ O	47.4	N/A	N/A	2.0 – 13.0	N/A	21	N/A	N/A		[10]
		Al ₂ O ₃	RuO ₂ , La ₂ O ₃	49.3	N/A	N/A	2.0 – 12.0	N/A	19	N/A	N/A	Ag AgCl KCl	[11]
		Al ₂ O ₃	RuO ₂ , TiO ₂	56.6	630	0.999	2.0 – 11.0	15	N/A	5	N/A		[12]
		Al ₂ O ₃ -Pt	RuO ₂	58.0	640	N/A	2.0 – 13.0	1-2	23	~ 0	1.5		[13]
	RuO ₂ -Nafion	Al ₂ O ₃	RuO ₂	58.3	656	0.999	2.0 – 12.0	42	22	N/A	0.4		[5]
	RuO ₂ -Nafion	Al ₂ O ₃	RuO ₂ -glass ⁴	58.6	684	0.995	3.0 – 11.0	N/A	N/A	11.5 – 26	N/A		[14]

Deposition method	Electrode sensitive material	Substrate	Precursor	Slope, mV/pH	E ⁰ , mV	R ²	pH range	Response time, s	T, °C	Hysteresis, mV	Drift, mV/h	Reference electrode	Ref.
Sol-gel	RuO ₂ -CN	Au, Co, steel	RuO ₂ , CNT	63.1	647	1.000	2.0 – 12.0	50	N/A	N/A	N/A	SCE	[15]
Pechini	RuO ₂ -TiO ₂	Ti	RuCl ₃ , Ti	56.0	N/A	0.998	2.0 – 12.0	N/A	25	N/A	N/A		[16]
RFMS ⁵	RuO ₂	Pt wire	RuO ₂ -glass ⁶	60	913	N/A	2.0 – 12.0	90	25	30	3	NHE	[17]
		OMC ⁷	RuO ₂	57.8	598	0.999	2.0 – 12.0	180	22	3.14	19.0	Ag AgCl KCl	[18]
		OMC	RuO ₂	58.4	670	0.999	4.0 – 10.0	30	22	1.13	5.0		[19]
		Carbon	RuO ₂	59.2	800	1.000	4.0 – 10.0	25	22	5.44	20.5		[19]
		Pt	RuO ₂	58.6	925	0.999	4.0 – 10.0	20	22	6.45	23.4		[19]
		Si	Ru	55.6	N/A	N/A	1.0 – 13.0	<1	N/A	4.36	0.38	SCE	[20]
		Si	Ru	51.7	N/A	0.978	2.0 – 10.0	N/A	N/A	N/A	N/A		[21]
		Si	RuO ₂	55.8	N/A	0.998	2.0 – 10.0	N/A	N/A	N/A	N/A	Ag AgCl KCl	[21]
		Si	Ru	56.0	N/A	N/A	1.0 - 12.0	N/A	N/A	N/A	N/A		[22]
		Al ₂ O ₃	RuO ₂	73.8	N/A	0.998	4.0 - 10.0	3	22	~ 5	N/A	RuO ₂ ⁸	[23]
		Al ₂ O ₃	RuO ₂	58.8	N/A	0.999	2.0 – 12.0	30	22	1.3	2.9		[24]
	RuO ₂ -Ta ₂ O ₅ -Nafion	Al ₂ O ₃	RuO ₂	55.3	288	1.000	2.0 – 12.0	136 (pH 6)	22	0.7	7.2	RuO ₂ ⁸	[24]
	RuO ₂ -CNT ⁹	Ta	Ru, CNT	55.5	643	1.000	2.0 – 12.0	40	25	10.2	~ 3	Ag AgCl KCl	[25]

¹ ED – Electrodeposition

² NHE – Normal Hydrogen Electrode

³ SCE – Saturated calomel electrode

⁴ RuO₂-glass paste with the resistivity of 10 kΩ/sq (3914, Electro-Science Laboratories, USA)

⁵ RFMS – Radio-Frequency Magnetron Sputtering

⁶ Submicron particles of RuO₂ and high lead silicate, or borosilicate, glass (typically containing 63-90% PbO, 10-25% SiO₂ and 0-25% B₂O₃, by weight) dispersed in a viscous organic liquid This study

⁷ OMC - Ordered Mesoporous Carbon

⁸ RuO₂, acrylic well filled with PVB-SiO₂ junction material

⁹ CNT – Carbon Nanotubes

Table S2. Change of the sensitivity of the fabricated electrodes with time

Time, days	Temperature, ° C	Theoretical sensitivity, mV/pH	Measured sensitivity, mV/pH		
			RuO ₂ -800	RuO ₂ -850	RuO ₂ -900
1	21	58.3	61.8 ± 1.0	60.5 ± 1.4	56.1 ± 2.1
3	21	58.3	60.0 ± 1.5	58.1 ± 0.4	59.4 ± 0.7
6	22	58.5	58.3 ± 0.0	59.5 ± 0.6	59.3 ± 0.0
7	22	58.5	62.0 ± 0.1	62.1 ± 0.6	59.8 ± 0.1
11	22	58.5	60.6 ± 0.3	58.5 ± 1.8	59.3 ± 1.8
14	24	58.9	58.7 ± 0.3	58.9 ± 0.3	62.2 ± 0.5

References

- Pasztor, K.; Sekiguchi, A.; Shimo, N.; Kitamura, N.; Masuhara, H. Electrochemically-deposited RuO₂ films as pH sensors. *Sens. Actuators B Chem.* **1993**, *14*, 561–562, doi:10.1016/0925-4005(93)85091-n.
- Shim, J.H.; Kang, M.; Lee, Y.; Lee, C. A nanoporous ruthenium oxide framework for amperometric sensing of glucose and potentiometric sensing of pH. *Microchim. Acta* **2012**, *177*, 211–219, doi:10.1007/s00604-012-0774-9.
- Mingels, R.; Kalsi, S.; Cheong, Y.; Morgan, H. Iridium and Ruthenium oxide miniature pH sensors: Long-term performance. *Sens. Actuators B Chem.* **2019**, *297*, 126779, doi:10.1016/j.snb.2019.126779.
- Koncki, R.; Mascini, M. Screen-printed ruthenium dioxide electrodes for pH measurements. *Anal. Chim. Acta* **1997**, *351*, 143–149, doi:10.1016/s0003-2670(97)00367-x.
- Uppuluri, K.; Lazouskaya, M.; Szwagierczak, D.; Zaraska, K. Influence of temperature on the performance of Nafion coated RuO₂ based pH electrodes. In Proceedings of the 2021 IEEE International Conference on Flexible and Printable Sensors and Systems (FLEPS), Manchester, UK, 20–23 June 2021; pp. 1–4.
- Mihell, J.; Atkinson, J. Planar thick-film pH electrodes based on ruthenium dioxide hydrate. *Sens. Actuators B Chem.* **1998**, *48*, 505–511, doi:10.1016/s0925-4005(98)00090-2.
- Manjakkal, L.; Synkiewicz, B.; Zaraska, K.; Cvejín, K.; Kulawik, J.; Szwagierczak, D. Development and characterization of miniaturized LTCC pH sensors with RuO₂ based sensing electrodes. *Sens. Actuators B Chem.* **2016**, *223*, 641–649, doi:10.1016/j.snb.2015.09.135.
- Manjakkal, L.; Cvejín, K.; Kulawik, J.; Zaraska, K.; Socha, R.P.; Szwagierczak, D. X-ray photoelectron spectroscopic and electrochemical impedance spectroscopic analysis of RuO₂-Ta₂O₅ thick film pH sensors. *Anal. Chim. Acta* **2016**, *931*, 47–56, doi:10.1016/j.aca.2016.05.012.
- Manjakkal, L.; Cvejín, K.; Kulawik, J.; Zaraska, K.; Szwagierczak, D.; Stojanovic, G. Sensing mechanism of RuO₂-SnO₂ thick film pH sensors studied by potentiometric method and electrochemical impedance spectroscopy. *J. Electroanal. Chem.* **2015**, *759*, 82–90, doi:10.1016/j.jelechem.2015.10.036.
- Zhuiykov, S.; Kats, E.; Marney, D.; Kalantar-Zadeh, K. Improved antifouling resistance of electrochemical water quality sensors based on Cu₂O-doped RuO₂ sensing electrode. *Prog. Org. Coat.* **2011**, *70*, 67–73, doi:10.1016/j.porgcoat.2010.10.003.
- Zhuiykov, S.; Kats, E.; Marney, D.; Kalantar-Zadeh, K. Improved antifouling resistance of electrochemical water quality sensors based on Cu₂O-doped RuO₂ sensing electrode. *Prog. Org. Coat.* **2011**, *70*, 67–73, doi:10.1016/j.porgcoat.2010.10.003.
- Manjakkal, L.; Cvejín, K.; Kulawik, J.; Zaraska, K.; Szwagierczak, D.; Socha, R.P. Fabrication of thick film sensitive RuO₂-TiO₂ and Ag/AgCl/KCl reference electrodes and their application for pH measurements. *Sens. Actuators B Chem.* **2014**, *204*, 57–67, doi:10.1016/j.snb.2014.07.067.
- Zhuiykov, S. Morphology of Pt-doped nanofabricated RuO₂ sensing electrodes and their properties in water quality monitoring sensors. *Sens. Actuators B Chem.* **2009**, *136*, 248–256, doi:10.1016/j.snb.2008.10.030.
- Lazouskaya, M.; Tamm, M.; Scheler, O.; Uppuluri, K.; Zaraska, K. Nafion as a protective membrane for screen-printed pH-sensitive ruthenium oxide electrodes. In Proceedings of the 2020 17th Biennial Baltic Electronics Conference (BEC), Tallinn, Estonia, 6–8 October 2020; pp. 1–4.
- Kahram, M.; Asnavandi, M.; Dolati, A. Synthesis and electrochemical characterization of sol-gel-derived RuO₂/carbon nanotube composites. *J. Solid State Electrochem.* **2013**, *18*, 993–1003, doi:10.1007/s10008-013-2346-2.
- Pocriška, L.; Gonçalves, C.; Grossi, P.; Colpa, P.; Pereira, E. Development of RuO₂-TiO₂ (70–30)mol% for pH measurements. *Sens. Actuators B Chem.* **2006**, *113*, 1012–1016, doi:10.1016/j.snb.2005.03.087.
- McMurray, H.; Douglas, P.; Abbot, D. Novel thick-film pH sensors based on ruthenium dioxide-glass composites. *Sens. Actuators B Chem.* **1995**, *28*, 9–15, doi:10.1016/0925-4005(94)01536-q.
- Lonsdale, W.; Wajrak, M.; Alameh, K. Effect of conditioning protocol, redox species and material thickness on the pH sensitivity and hysteresis of sputtered RuO₂ electrodes. *Sens. Actuators B Chem.* **2017**, *252*, 251–256, doi:10.1016/j.snb.2017.05.171.

19. Lonsdale, W.; Maurya, D.; Wajrak, M.; Alameh, K. Effect of ordered mesoporous carbon contact layer on the sensing performance of sputtered RuO₂ thin film pH sensor. *Talanta* **2017**, *164*, 52–56, doi:10.1016/j.talanta.2016.11.020.
20. Liao, Y.-H.; Chou, J.-C. Preparation and characteristics of ruthenium dioxide for pH array sensors with real-time measurement system. *Sens. Actuators B Chem.* **2008**, *128*, 603–612, doi:10.1016/j.snb.2007.07.023.
21. Yao, X.; Vepsäläinen, M.; Isa, F.; Martin, P.; Munroe, P.; Bendavid, A. Advanced RuO₂ Thin Films for pH Sensing Application. *Sensors* **2020**, *20*, 6432, doi:10.3390/s20226432.
22. Chou, J.-C.; Liu, S.-I.; Chen, S.-H. Sensing Characteristics of Ruthenium Films Fabricated by Radio Frequency Sputtering. *Jpn. J. Appl. Phys.* **2005**, *44*, 1403–1408, doi:10.1143/jjap.44.1403.
23. Sardarinejad, A.; Maurya, D.K.; Alameh, K. The pH Sensing Properties of RF Sputtered RuO₂ Thin-Film Prepared Using Different Ar/O₂ Flow Ratio. *Materials* **2015**, *8*, 3352–3363, doi:10.3390/ma8063352.
24. Lonsdale, W.; Wajrak, M.; Alameh, K. Manufacture and application of RuO₂ solid-state metal-oxide pH sensor to common beverages. *Talanta* **2018**, *180*, 277–281, doi:10.1016/j.talanta.2017.12.070.
25. Xu, B.; Zhang, W.-D. Modification of vertically aligned carbon nanotubes with RuO₂ for a solid-state pH sensor. *Electrochim. Acta* **2010**, *55*, 2859–2864, doi:10.1016/j.electacta.2009.12.099.