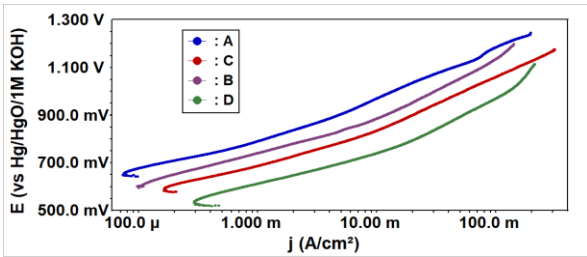

Figure 7: Tafel plots for oxygen evolution on $Ni/Sm_{1-x}Sr_xNiO_3$ ($0 \leq x \leq 0.8$) in 1M KOH at 25 ˚C (scan rate: 0.2 $mVsec^{-1}$).
A: $SmNiO_3$, B: $Sm_{0.8}Sr_{0.2}NiO_3$, C: $Sm_{0.6}Sr_{0.4}NiO_3$,
D: $Sm_{0.2}Sr_{0.8}NiO_3$

Table 2: Electrode kinetic parameters for oxygen evolution reaction on $Ni/Sm_{1-x}Sr_xNiO_3$ ($0 \leq x \leq 0.8$) electrodes in 1 M KOH at 25°C

Electrode	Tafel slope (b)	Order (p)	E/ mV at j/ mA cm^{-2}		j/ mA cm^{-2} at E/ mV	
			10	100	700	800
$SmNiO_3$	118	1.9	921	1134	0.5	1.1
$Sm_{0.8}Sr_{0.2}NiO_3$	113	1.2	849	1068	0.9	1.5
$Sm_{0.6}Sr_{0.4}NiO_3$	114	0.9	888	1116	0.9	1.3
$Sm_{0.2}Sr_{0.8}NiO_3$	111	1.0	815	1045	1.2	4.1

As per Table 2, oxide electrodes show the following order of electrocatalytic activity at constant potential (E = 800 mV);

$Sm_{0.2}Sr_{0.8}NiO_3$ (j = 4.1 mA cm^{-2}) > $Sm_{0.8}Sr_{0.2}NiO_3$ (j = 1.5 mA cm^{-2}) > $Sm_{0.6}Sr_{0.4}NiO_3$ (j = 1.3 mA cm^{-2}) > $SmNiO_3$ (j = 1.1 mA cm^{-2})

The anodic polarization curve was recorded to determine the reaction order of OE with each oxide electrode in different KOH concentraation at 25°C. During the process, the electrical intensity of the each electrolytic solution was kept uniform. An inert electrolyte KNO_3 was used to maintain the ionic strength (µ = 1.5) of each solution constant. A representative polarization curve for $Ni/Sm_{0.2}Sr_{0.8}NiO_3$ is shown in the Fig. 8. From figure, values of current density (log j/ A cm^{-2}) were estimated at a certain potential and plotted against log [OH^-] , which is shown in the Fig. 9 at a constant potential of E=700 mV. The order of reaction was calculated by measuring the slope of straight line and values are listed in Table 2. The observed values of Tafel slope and reaction order as given in Table 2 suggest that the OER taking place at the electrocatalysts follows similar mechanistic path except $SmNiO_3$, which has reaction order 1.9 with Tafel slope 118 mV $decade^{-1}$.

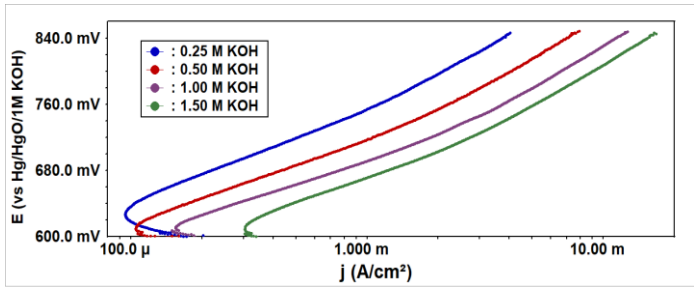

Figure 8: Tafel plots for oxygen evolution on $Ni/Sm_{0.2}Sr_{0.8}NiO_3$ at varying KOH concentrations (µ = 1.5) at 25 ˚C

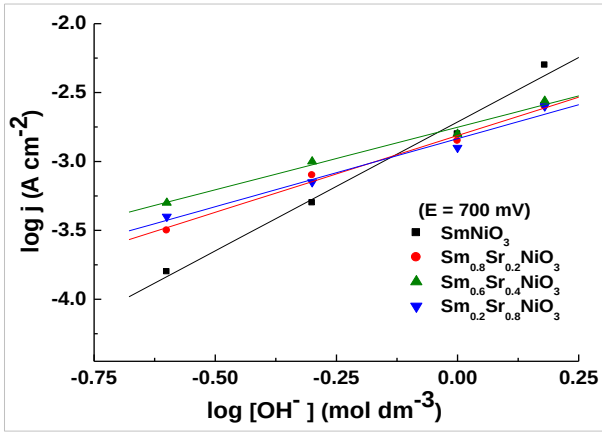

Figure 9: Plot of log j vs log [OH^-] for $Ni/Sm_{1-x}Sr_xNiO_3$ ($0 \leq x \leq 0.8$) electrodes.

3.5 Thermodynamic Parameters

Thermodynamic parameters of two oxide electrocatalysts towards OER have also been determined by recording the anodic polarization curve in 1 M KOH at 20, 30, 40, and 50°C. A set of polarization curve for $SmNiO_3$ is shown in Figure 10. During the experiment, the temperature of the reference electrode was kept constant. From figure, values of log j (in mA cm^{-2}) were estimated at a constant applied potential and plotted against 1/T. The standard apparent enthalpy of activation ($\Delta H_{el}^{\circ\#}$) was calculated at a certain potential (E = 650 mV) by measuring the slope of Arrhenius plot, log j vs 1/T (Fig. 11).

Further, following two relations (1) and (2) [53] are used to determine the values of standard enthalpy of activation ($\Delta H^{\circ\neq}$) and standard entropy of activation ($\Delta S^{\circ\neq}$), respectively.

$$\Delta H_{el}^{\circ\neq} = \Delta H^{\circ\neq} - \alpha F\eta \qquad \ldots\ldots (1)$$

$$\Delta S^{\circ\neq} = 2.3R\left[\log j + \frac{\Delta H_{el}^{\circ\neq}}{2.3RT} - \log (nF\omega C_{OH^-})\right] \qquad \ldots\ldots (2)$$

In equation (1), α (= 2.303RT/bF) is the transfer coefficient. η is the overpotential equal to E - E_{O_2/OH^-}, where E is the potential applied and E_{O_2/OH^-} (= 0.303 V vs. Hg/HgO) [54] is the theoretical equilibrium Nernst potential in 1 M KOH at 25 ˚C. The Tafel slope (b) is determined from the polarization curves obtained at different temperatures. R, F are the universal constants and T is the absolute temperature.

In equation (2), the value of frequency term (ω) is equal to k_BT/h. k_B and h are the Boltzmann constant and Planck's constant, respectively. Here, the value of 'n' was taken 2 in every calculation. The calculated values of thermodynamic parameters are listed in the Table 3. Values of electrochemical activation energy were found to be 47.5 and 54.9 kJ mol^{-1} for $SmNiO_3$ and $Sm_{0.8}Sr_{0.2}NiO_3$, respectively.

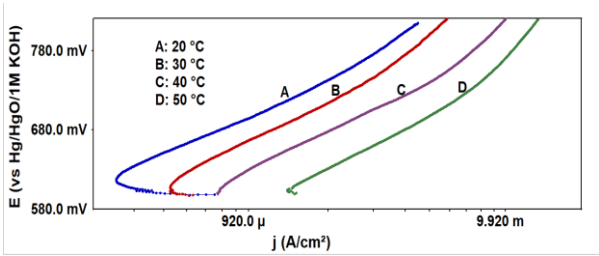

Figure 10: Anodic polarization curve for the $SmNiO_3$ film electrode on Ni at different temperatures in 1 M KOH

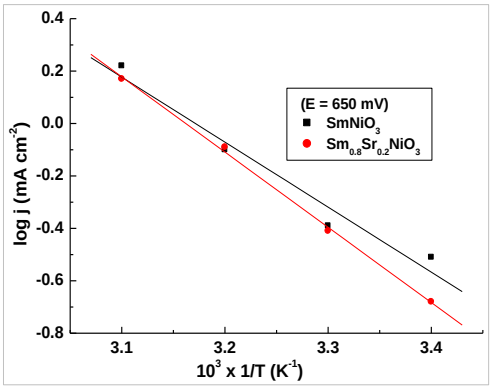

Figure 11: The Arrhenius plot at a constant applied potential (650 mV) for La1-xSrxCoO3 (x = 0 and 0.2) in 1 M KOH

Table 3: Thermodynamic parameters for O_2 evolution on $Ni/Sm_{1-x}Sr_xNiO_3$ (x = 0 and 0.2) in 1 M KOH

Electrode	$\Delta H_{el}^{\circ\#}$ (kJ mol^{-1})	$-\Delta S^{\circ\#}$ ($Jdeg^{-1}$ mol^{-1})	α	$\Delta H^{\circ\#}$ (kJ mol^{-1})
$SmNiO_3$	47.5	195.1	0.5	64.4
$Sm_{0.8}Sr_{0.2}NiO_3$	54.9	171.9	0.5	71.5

CONCLUSION

The present work has been undertaken to study the electrocatalytic properties of Sm-based perovskite over La-based. Sr-substitution in the base oxide increased the electrocatalytic properties of the material. But, this increase is not so significant as observed in the case of La-based perovkites. As per present study, Sm-based perovskites are not prolific electrocatalysts for the electrolysis point of view.

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REFERENCES

1. Meadocroft D. B. (1970). Low-cost oxygen electrode material, Nature, 226:847-848. https://doi.org/10.1038/226847a0.
2. Matsumoto Y., Sato E. (1979). Oxygen evolution on $La_{1-x}Sr_xMnO_3$ electrodes in alkaline solutions, Electrochim. Acta, 24:421-423. https://doi.org/10.1016/0013-4686(79)87030-9.
3. Matsumoto Y., Yamada S., Nishida T., Sato E. (1980). Oxygen evolution on $La_{1-x}Sr_xFe_{1-y}Co_yO_3$ series oxides, J. Electrochem. Soc., 127:2360-2364. https://doi.org/10.1149/1. 2129415.
4. Yamada S., Matsumoto Y., Sato E. (1981). Oxygen Evolution on $La_{1-x}Sr_xFe_{1-y}Ni_yO_3$ Series Oxides, The journal of the Electrochemical Society of Japan, 49:269-273. https://doi.org/10.5796/kogyobutsurikagaku.49.269
5. Kobussen A.G.C., Willems H., Broers G.H.J. (1982). The oxygen evolution on $La_{0.5}Ba_{0.5}CoO_3$: Passivation processes, J. Electroanalytical Chemistry and Interfacial Electrochemistry 142:85-94. https://doi.org/10.1016/S0022-0728(82)80007-7
6. Bockris J. O'M, Otagawa T., Young V. (1983). Solid state surface studies of the electrocatalysis of oxygen evolution on perovskites, J. Electroanal. Chem., 150:633-643. https://doi.org/10.1016/S0022-0728(83)80243-5.
7. Shimizu Y., Matsuda H., Miura N., Yamazoe N. (1992). Bi-functional Oxygen Electrode Using Large Surface Area Perovskite-type Oxide Catalyst for Rechargeable Metal-Air Batteries, Chem. Lett., 21:1033-1036. https://doi.org/10.1246/cl.1992.1033.
8. Schmidt T., Wendt H. (1994). Electrocatalysis of cathodic hydrogen and anodic oxygen evolution in alkaline water electrolysis by in situ activation procedures, Electrochim. Acta., 39:1763-1767. https://doi.org/10.1016/00134686(94)85162-X.
9. Tiwari S. K., Chartier P., Singh R. N.(1995). Preparation of Perovskite-Type Oxides of Cobalt by the Malic Acid Aided Process and Their Electrocatalytic Surface Properties in Relation to Oxygen Evolution, J. Electrochem. Soc., 143:148-153. https://doi.org/10.1149/1.2043854.
10. Jain A. N., Tiwari S. K., Singh R. N. Chartier P. (1995). Low-temperature synthesis of perovskite-type oxides of lanthanum and cobalt and their electrocatalytic properties for oxygen evolution in alkaline solutions, J. Chem. Soc. Faraday Trans., 91:1871-1875. https://doi.org/10.1039/FT9959101871.
11. Singh R. N., Bahadur L., Pandey J. P., Singh S. P., Chartier P., Poillerat G. (1994). Preparation and characterization of thin films of $LaNiO_3$ for anode application in alkaline water electrolysis, J. Appl. Electrochem., 24:149-156. https://doi.org/10.1007/BF00247787.
12. Singh S. P., Singh R. N., Poillerat G., Chartier P. (1995), Physicochemical and electrochemical characterization of active films of $LaNiO_3$ for use as anode in alkaline water electrolysis, Int. J. Hydrogen Energy, 20:203-210. https://doi.org/10.1016/0360-3199(94)E0027-V.
13. Singh R. N., Jain A. N., Tiwari S. K., Poillerat G., Chartier P. (1995). Physicochemical and electrocatalytic properties

of $LaNiO_3$ prepared by a low-temperature route for anode application in alkaline water electrolysis., *J. Appl. Electrochem*., 25:1133-1138. https://doi.org/10.1007/BF00242541.

14. Tiwari S. K., Koenig J. F., Poillerat G., Chartier P., Singh R. N. (1998). Electrocatalysis of oxygen evolution/ reductionon $LaNiO_3$ prepared by a novel malic acid-aided method, J. Appl. Electrochem., 28:114-119. https://doi.org/10.1023/A:1003214321780.
15. Singh R. N., Tiwari S. K., Singh S. P., Singh N. K., Poillearat G., Chartier P. (1996). Synthesis of (La, Sr)CoO_3 perovskite films via a sol–gel route and their physicochemical and electrochemical surface characterization for anode application in alkaline water electrolysis, J. Chem. Soc. Faraday Trans., 92(14):2593-2597. https://doi.org/10.1039/FT9969202593.
16. Singh R. N., Tiwari S. K., Singh S. P., Jain A. N., Singh N. K. (1997). Electrocatalytic activity of high specific surface area perovskite-type $LaNiO_3$ via sol-gel route for electrolytic oxygen evolution in alkaline solution, Int. J. Hydrogen Energy, 22:557-562. https://doi.org/10.1016/S0360-3199(96)00176-0.
17. Sharma T., Singh N. K., Tiwari S. K., Singh R. N. (1998). Electrocatalytic properties of La-manganites prepared by low temperature synthesis, Ind. J. Engg. & Mat. Sci., 5:38-42.
18. Singh N. K., Tiwari S. K., Singh R. N. (1998). Electrocatalytic properties of lanthanum manganites obtained by a novel malic acid-aided route, Int. J. Hydrogen Energy, 23:775-780. https://doi.org/10.1016/S0360-3199(97)00119-5.
19. Lal B., Singh N. K., Singh R. N. (2001). Electrocatalytic properties of Sr-doped $LaMnO_3$ obtained by a new sol-gel route in relation to O_2 evolution in alkaline solution, Ind. J. Chem., 40 A:1269-1276.
20. Singh N. K., Lal B., Singh R. N. (2002). Electrocatalytic properties of perovskite-type $La_{1-x}Sr_xMnO_3$ obtained by a novel sol–gel route for O_2 evolution in KOH solutions, *Int.* J. Hydrogen Energy, 27:885-893. https://doi.org/10.1016/S0360-3199(02)00008-3.
21. Lal B., Raghunanda M. K., Gupta M., Singh R. N. (2005). Electrocatalytic properties of $La_{1-x}Sr_xCoO_3(0 \leq x \leq 0.4)$ perovskite-type obtained by a novel stearic acid sol–gel method for electrocatalysis of O_2 evolution in KOH solutions *Int. J. Hydrogen Energy*, 30:723-729. https://doi.org/10.1016/j.ijhydene.2004.07.002.
22. Suntivich J., Gasteiger H. A., Yabuuchi N., Nakanish H., Goodenough J. B., Shao-Horn Y. (2011). Design principles for oxygen-reduction activity on perovskite oxide catalysts for fuel cells and metal–air batteries, Nature Chemistry, 3:546-550. https://doi.org/10.1038/nchem.1069
23. Sunarso J., Torriero A. A. J., Zhou W., Howlett P. C., Forsyth M. (2012). Oxygen Reduction Reaction Activity of La-Based Perovskite Oxides in Alkaline Medium: A Thin-Film Rotating Ring-Disk Electrode Study, J. Phys. Chem., 116:5827-5834. https://doi.org/10.1021/jp211946n.
24. Yadav M. K., Yadav Ritu, Sharma Priya, Singh N. K. (2016). Synthesis and electrocatalytic properties of $La_{1-x}Sr_xCoO_3$ $(0 \leq x \leq 0.8)$ film electrodes for oxygen evolution in alkaline solutions, Int. J. Electrochem. Sci., 11:8633-8645. doi: 10.20964/2016.10.01.
25. Singh N. K., Yadav M. K., Fernandez C. (2017). Electrocatalytic properties of $La_{1-x}Cu_xCoO_3$ $(0 \leq X \leq 0.8)$ film electrodes prepared by malic acid sol-gel method at pH =3.75, Int. J. Electrochem Sci., 12:7128-7141. doi: 10.20964/2017.08.68.
26. Singh N. K., Sharma P., Kumar I., Chaddha A. S. (2019). Oxygen evolution electrocatalytic properties of perovskite-type $La_{1-x}Sr_xCoO_3$ $(0 \leq x \leq 0.8)$ oxides obtained by polyvinylpyrrolidone sol-gel route, Int. J. Electrochem. Sci., 14:11379-11390. doi: 10.20964/2019.12.70.
27. Singh N. K., Sharma P., Yadav M. K., Parihar R. (2020). Oxygen evolution electrocatalytic properties of perovskite-type oxides obtained by PVP sol-gel route: Part II. The effect of partial substitution of Sm for Sr in $La_{0.4}Sr_{0.6}CoO_3$, Int. J. Electrochem. Sci., 15:7001-7012. doi:10.20964/2020.07.81.
28. Shin Boyoon, Choi Sangwon, Tak Yongsug (2016). Electrocatalytic Activity of Co-based Perovskite Oxides for Oxygen Reduction and Evolution Reactions, *Int. J. Electrochem. Sci*., 11:5900-5908, https://doi.org/10.20964/2016.07.68.
29. Zhang Z., Zhou D., Wu X., Bao X., Liao J., Wen M. 2019). Synthesis of $La_{0.2}Sr_{0.8}CoO_3$ and its electrocatalytic activity for oxygen evolution reaction in alkaline solution, *Int. J. Hydrogen Energy*, 44:7222-7227, https://doi.org/10.1016/j.ijhydene.2019.01.268
30. Singh R. N., Lal B. (2002). High surface area lanthanum cobaltate and its A and B sites substituted derivatives for electrocatalysis of O_2 evolution in alkaline solution, *Int. J. Hydrogen Energy*, 27:445-46, https://doi.org/10.1016/S0360-3199(01)00078-7
31. Tseung A. C. C., Bevan H. L. (1973). A reversible oxygen electrode, J. Electroanal. Chem., 45:429-438. https://doi.org/10.1016/S0022-0728(73)80053-1.
32. Matsuki K., Kamada H. (1985). Research on Energy Conversion and Storage Through Chemical Process, SPEY, vol. 13 p. 181.
33. Bockris J. O. M., Otagawa T. (1984). The Electrocatalysis of oxygen evolution on perovskites, J. Electrochem. Soc., 131: 290-302. https://doi.org/10.1149/1.2115565.
34. Balej J. (1985). Electrocatalysts for oxygen evolution in advanced water electrolysis, Int. J. Hydrogen Energy, 10:89-99. https://doi.org/10.1016/0360-3199(85)90041-2.
35. Kobussen A. G. C., Buren van F. R., Den Belt van T. G. M., Wees van H. J. A. (1979). Oxygen evolution on $LaCoO_3$-type electrodes, *J. Electroanal Chem*., 96:123-125.
36. Matsumoto Y., Manabe H., Sato E. (1980). Oxygen evolution on $La_{1-x}Sr_xCoO_3$ electrodes in alkaline solutions, J. Electrochem Soc. 127:811-814. https://doi.org/10.1149/1.2129762
37. Wendt H., Plzak V. (1983). Electrocatalytic and thermal activation of anodic oxygen- and cathodic hydrogen-evolution in alkaline water electrolysis, Electrochim Acta, 28:27-34. https://doi.org/10.1016/0013-4686(83)85083-X.
38. Fiori G., Mari C. M. (1982). Electrocatalysis of oxygen evolution, Int. J. Hydrogen Energy, 7:489-493. https://doi.org/10.1016/0360-3199(82)90106-9.
39. Vidyasagar K., Gopalkrishnan J., Rao C.N.R. (1985). Synthesis of complex metal oxides using hydroxide, cyanide, and nitrate solid solution precursors, J. Solid state chem., 58:29-37. https://doi.org/10.1016/0022-4596(85)90266-x
40. Vassiliou J. K., Hornbostel M., Ziebarth R., Disalvo F. J. (1989). Synthesis and properties of $NdNiO_3$ prepared by

low-temperature methods, J. Solid State Chem., 81:208-216. https://doi.org/10.1016/0022-4596(89)90008-X
41. Teraoka Y., Kakebayashi H., Moriguchi I., Kagawa S. (1991). Hydroxy acid-aided synthesis of perovskite-type oxides of cobalt and manganese, Chemistry Letters, 20:673-676. https://doi.org/10.1246/cl.1991.673
42. Taguchi H., Yoshioka H., Matsuda D., Nagao M. (1993). Crystal structure of $LaMnO_{3+\delta}$ synthesized using poly (acrylic acid), Solid State Chem., 104:460-463. https://doi.org/10.1006/jssc.1993.1181.
43. Nagai T., Fujiwara N., Asahi M., Yamazaki Shin-Ichi, Siroma Z., Ioroi T. (2014). Synthesis of nano-sized perovskite-type oxide with the use of polyvinyl pyrrolidone, J. Asian Ceramic Society, 2:329-332. https://doi.org/10.1016/j.jascer.2014.08.004
44. Azad Uday Pratap, Singh Monika, Ghosh Sourav, Singh Ashish Kumar, Ganesan Vellaichamy, Singh Akhilesh Kumar, Prakash Rajiv (2018). Facile synthesis of BSCF perovskite oxide as an efficient bifunctional oxygen electrocatalyst, Int. J. Hydrogen Energy, 43:20671-20679. https://doi.org/10.1016/j.ijhydene.2018.09.134
45. Gozzo C. B., Mario R. S. Soares, Sczancoski J. C., Nogueira I. C. , Edson R. Leite. (2019). Investigation of the electrocatalytic performance for oxygen evolution reaction of Fe-doped lanthanum nickelate deposited on pyrolytic graphite sheets *Int. J. Hydrogen Energy,* 39:21659-21672. https://doi.org/10.1016/j.ijhydene.2019.06.109
46. Grimaud Alexis, May Kevin J., Carlton Christopher E., Lee Yueh-Lin, Risch Marcel, Hong Wesley T., Zhou Jigang, Shao-Horn Y. (2013). Double perovskites as a family of highly active catalysts for oxygen evolution in alkaline solution, Nature Communications, 4:1-7. https://doi.org/10.1038/ncomms3439.
47. Fradette N., Marsan B. (1998). Surface studies of $Cu_xCo_{3-x}O_4$ electrodes for the electrocatalysis of oxygen evolution, J. Electrochem. Soc., 145:2320-2327, https://doi.org/10.1149/1.1838637.
48. Singh R. N., Pandey J. P., Anitha K. L. (1993). Preparation of electrodeposited thin films of nickel-iron alloys on mild steel for alkaline water electrolysis. Part I: studies on oxygen evolution, Int. J. Hydrogen Energy, 18:467-473. https://doi.org/10.1016/0360-3199(93)90002-R
49. Singh N. K., Tiwari S. K., Anitha K. L., Singh R. N. (1996). Electrocatalytic properties of spinel-type $Mn_xFe_{3-x}O_4$ synthesized below 100°C for oxygen evolution in KOH solutions, J. Chem. Soc. Faraday Trans., 92(13):2397-2400. https://doi.org/10.1039/FT9969202397.
50. Wu Wei, Guo Shaoqiang, Zhang Jinsuo (2018). Electrochemical Behaviors of Cr(III) in Molten LiF-NaF-KF Eutectic, Int. J. Electrochem. Sci., 13:225-234. doi: 10.20964/2018.01.21.
51. Massot L., Chamelot P., Cassayre L., Taxil P. (2009). Electrochemical study of the Eu(III)/Eu(II) system in molten fluoride media, Electrochim Acta, 54:6361-6366. https://doi.org/10.1016/j.electacta.2009.06.016.
52. Bard A. J., Faulkner L. R. (2001). Electrochemical Methods: Principles and Applications, 2nd ed., Wiley, New York.
53. Gileadi E. (1993). Electrode Kinetics, (VCH Publishers Inc., New York), p.151.
54. Singh R. N., Pandey J. P., Singh N. K., Lal B., Chartier P., Koenig J. F. (2000). Sol-gel derived spinel $M_xCo_{3-x}O_4$ (M = Ni, Cu; $0 \leq x \leq 1$) films and oxygen evolution, Electrochim Acta, 45:1911-1919, https://doi.org/10.1016/S00134686 (99)00413-2