Journal of Advances in Physical Chemistry 物理化学进展, 2024, 13(2), 165-174
Published Online May 2024 in Hans. https://www.hanspub.org/journal/japc
https://doi.org/10.12677/japc.2024.132020

Hans汉斯

LDH中引入氧空位用于电催化和和超级电容器的研究进展

李天鹏

上海理工大学材料与化学学院，上海

收稿日期：2024年4月6日；录用日期：2024年5月23日；发布日期：2024年5月31日

摘　要

对清洁能源的迫切需求和现代电子技术的快速发展促使人们对绿色能源和新型储能技术的关注越来越多，尤其是电化学水分解和超级电容器。而最重要的是设计具有优良催化和储能性能的电极材料。层状双金属氢氧化物(LDHs)由于其组成、结构和形态的易调性引起了研究人员的强烈兴趣，同时在LDH中引入氧空位以提升其催化和储能性能得到了广泛研究并取得了各种卓有成效的成果。本文综述了电催化和超级电容器用具有氧空位的LDH基电极材料设计和研究的最新进展。从氧空位的形成、氧空位对于电催化和储能性能的提升等方面进行了讨论。通过科学家们的不断努力，富氧空位的LDH基材料的催化性能和储能性能都有了很大的提高，使其在现代应用中更具竞争力。

关键词

层状双金属氢氧化物，氧空位，电催化，超级电容器

Progress in the Introduction of Oxygen Vacancies in LDH for Electrocatalysis and Supercapacitors

Tianpeng Li

School of Materials and Chemistry, University of Shanghai for Science and Technology, Shanghai

Received: Apr. 6th, 2024; accepted: May 23rd, 2024; published: May 31st, 2024

Abstract

With the urgent demand for clean energy and the rapid development of modern electronic tech-

文章引用: 李天鹏. LDH 中引入氧空位用于电催化和和超级电容器的研究进展[J]. 物理化学进展, 2024, 13(2): 165-174.
DOI: 10.12677/japc.2024.132020

nology, there is increasing attention on green energy and novel energy storage technologies, particularly electrochemical water splitting and supercapacitors. The design of electrode materials with excellent catalytic and energy storage performance is of paramount importance. Layered double hydroxides (LDHs) have attracted strong interest from researchers due to their tunability in composition, structure, and morphology. Meanwhile, the introduction of oxygen vacancies into LDHs to enhance their catalytic and energy storage performance has been widely studied, yielding various effective results. This review summarizes the latest progress in the design and research of LDH-based electrode materials with oxygen vacancies for electrocatalysis and supercapacitors. Discussions are provided on the formation of oxygen vacancies and their enhancement of electrocatalytic and energy storage performance. Through the continuous efforts of scientists, LDH-based materials rich in oxygen vacancies have shown significant improvements in catalytic and energy storage performance, making them more competitive in modern applications.

Keywords

Layered Double Hydroxides, Oxygen Vacancy, Electrocatalysis, Supercapacitor

1. 引言

全球人口的不断增长和化石燃料储备的枯竭共同引发了人们对环境的严重关切，并导致能源需求激增[1] [2]。煤炭和汽油消费产生的二氧化碳排放是导致全球变暖的因素之一，发展可持续和可再生能源对于解决人们对能源危机和环境污染的严重性日益增长的关注是紧迫和必要的，电化学储能和电化学水分解近年来受到广泛关注，成为开发利用新能源的关键[3]。

电化学水分解在获取氢气中起着至关重要的作用，它包括两个半反应：析氢反应(HER)和析氧反应(OER) [4]。其中 OER 是一个四电子传递过程，经常表现出缓慢的动力学和高过电位这些因素显著阻碍了电化学水分解技术的大规模制氢[5]。目前来说，具有良好 OER 和 HER 性能的非贵金属催化剂主要有层状双金属氢氧化物(LDHs)、过渡金属磷化物、硫化物、硒化物等[6] [7]。除此之外，要充分发挥新兴能源的潜力，就必须有一个经济高效的储能系统来调节不规则和间歇性的能源输出。因此，开发高效、便捷的储能技术和装置对于探索和利用新兴能源至关重要[8] [9]。超级电容器作为电化学储能设备，因其具有高功率密度、快速充放电能力和更长的循环寿命而受到广泛关注[10]。然而，超级电容器的能量密度相对较低，限制了其在长期能量存储方面的应用。此外，超级电容器的循环寿命和稳定性也需要进一步改善，以提高其可靠性和耐用性[11]。

层状双金属氢氧化物(LDH)是一种独特的二维层状纳米结构材料，其化学结构类似于$[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}_{x/n}\cdot mH_2O]$，其中 M^{2+}/M^{3+}和 A^{n-}分别表示二价/三价金属离子和层间阴离子。由于成分可控、环境友好且制备工艺相对简单，这种材料在多种应用领域都具有广阔的发展前景。大量的实验和理论研究证明，LDH 纳米片对析氧反应(OER)、析氢反应(HER)、氧还原反应(ORR)等多种电化学转化反应具有优异的催化性能[3] [12] [13]。同样的，由于其组成、结构和形态的可调性，LDH 材料用于超级电容器电极方面取得了各种卓有成效的成果[11] [14] [15]。

尽管 LDH 在电催化和超级电容器方面取得了很大的进展，但其导电性差、易堆叠、高电流密度下反应动力学迟缓以及循环稳定性弱等问题限制了其进一步应用。为了进一步增强 LDHs 的电化学性能，在

LDH 中引入缺陷，尤其是氧空位已经被证实可以大大提升 LDH 的电催化和储能性能。氧空位是指晶格由于缺少氧原子而产生的空位，会极大地改变电极材料的结构和电化学性能。在 LDH 中，氧空位的存在可提高导电性和活性位点，从而改善离子传输和电化学反应活性。研究人员发现，在 LDH 中引入氧空位后可以极大降低 OER 的过电位，大大提升 LDH 的电催化性能，其原因是改善了电荷转移，同时显著促进氢氧根离子的吸附，并改变含氧中间物种的吸附自由能[16]；同时，氧空位可产生丰富的不饱和配位位点和悬垂键，进一步调节活性金属位点周围的局部电子构型，从而提高 OER 的活性[17] [18] [19]。例如，Muhammad 等人使用 Ce 对 Co-Ni LDHs 进行掺杂引入氧空位，该方法显著增强了 OER 的活性[20]。除此之外，在储能方面，氧空位也显示出了极大的作用，由于 LDH 属于赝电容材料，依赖于氧化还原反应，但 LDH 往往受到其相对较差的导电性的限制，这阻碍了其超高理论容量的实现[21] [22]。氧空位会影响材料的电子结构、催化性能和离子扩散动力学[23] [24]，直接或间接导致材料的能带隙减小[25] [26]，进而影响材料的电导率。因此，引入氧空位是提高超级电容器电极材料性能的重要途径。

本综述在前人研究的基础上首先简述了 LDH 材料中引入氧空位的常用方法，然后系统介绍了近年来富氧空位 LDH 材料在电催化和超级电容器方向的研究进展以及氧空位对于材料性能的影响，以期为 LDH 材料的氧空位设计和研究奠定一定基础。

2. 产生氧空位的常用方法

2.1. 外源原子掺杂

原子掺杂是在 LDH 中引入氧空位最为常用的方法之一，主要是通过在合成过程中引入其他金属或非金属元素来实现。在掺杂时掺杂剂原子取代材料固有原子的晶格位点[15]。当掺杂剂掺入后，会导致原有原子的配位数发生改变，从而产生不饱和配位点和悬垂键，进而产生空位缺陷，这种方法可以改变材料的晶格结构和电子结构，从而影响其氧化还原性能和电化学活性[27]。主要用于改变材料的电学性质，如改变导电性、改变带隙能量等。掺杂引入氧空位有可调节性强，工艺简单的优点。近年来大量研究人员在 LDH 中掺杂其他金属元素从而引入氧空位，提升 LDH 的电催化和储能性能，Chen 等人研究了 Mg 掺杂的 Ni-LDH，通过镁的掺杂引入了大量的氧空位，所得的 NiMg-LDH 比原始 Ni-LDH 的 OER 过电位提升了 78 mV (η10) [28]；He 等人通过将钨掺入 NiFe-LDH 中引入了丰富的氧空位，并通过理论计算表明氧空位有效地调节了 FeNi-LDH 的本征电子结构，优化了中间体的吸附能，加速了 OER 反应动力学[26]。Ding 等人提出了一种钼(Mo)掺杂 NiCo-LDH 引入氧空位应用于高性能超级电容器的策略，通过密度泛函理论(DFT)计算了 LDH 电子结构和氧空位的调控，这表明 Mo 掺杂引入氧空位缩小了带隙，大大提升了储能性能[29]。

2.2. 等离子体刻蚀

等离子体刻蚀处理引入氧空位是一种表面处理技术，通过等离子体辉光放电或电弧放电等物理方法，将气体(N_2、Ar 等)激发为等离子体状态，利用高能粒子流轰击材料表面，引起材料表面变化，从而改变材料表面的物理、化学性质。在等离子体处理过程中，氧空位的形成主要是由于气体放电产生的高能粒子轰击材料表面，使得材料表面的氧原子被轰击离开表面，形成氧空位。等离子体刻蚀氧空位具有高精度、短时间和可控性好的优点。在过去的几年里，越来越多的研究人员利用等离子体刻蚀在 LDH 中引入氧空位，成功提升了其电化学性能[30]。Liu 等人利用 N_2 等离子体刻蚀 CoFe-LDH，引入了大量的缺陷和空位，导致 LDH 中具有更多的悬垂键和更大的比表面积，增加了反应活性位点，从而在碱性介质中获得了高活性的 HER 电催化剂[31]；Li 等人采用了空气等离子体处理 Ru 掺杂的 CoFe LDH，诱导电子相互作用和氧缺陷，从而调节电子结构，经空气等离子体处理的掺杂 Ru 的 CoFe LDH 的催化性能优于 CoFe LDH

和 RuO_2 催化剂[32]；等人提出了一种 V 掺杂与 H_2 等离子体还原相结合的策略，获得了富含氧空位的 V 掺杂 NiFe LDH 纳米片，激活了 NiFe LDH 纳米片阵列(NSA)的 HER 性能，通过氧空位和 NiV 的协同作用改善了电子结构，暴露了更多的活性位点，改善了电子转移路线，大大提升了 LDH 的催化性能[33]。

2.3. 氧化还原

通过氧化还原反应引入氧空位是最常见的方法之一。通常将制备好的 LDH 材料在氧化剂或还原剂中浸泡，在氧化剂或还原剂的作用下，LDH 的金属阳离子发生氧化或还原，导致氧空位的生成。常见的氧化剂和还原剂有过氧化氢和硼氢化钠等[34] [35]。通过氧化还原反应引入氧空位有可控性、强灵活性高的优电。Chen 等人通过正丁基锂还原处理 NiFe-LDH，通过深度还原和低温部分氧化来调节氧空位缺陷并改变 NiFe-LDH 的结晶性，获得的富氧空位的 NiFe-LDH 具有优异的催化性能[36]。Liang 使用化学还原法合成富氧空位的镍钴层状双金属氢氧化物纳米线阵列电极。还原剂为 $NaBH_4$ 溶液，在较温和的条件下产生氧空位，从而避免对氢氧化物的任何破坏。合成后的电极相对于原始 LDH 容量和稳定性都有了较大提升[35]。

3. 富氧空位的 LDH 在电催化和超级电容器方面的应用

3.1. 富氧空位的 LDH 在电催化方面的应用

电化学水分解是一种获得绿色能源氢的卓越技术，可用于未来的取代化石燃料，然而电化学水分解分为两个半反应：析氢反应(HER)和析氧反应(OER)，由于 OER 通常发生在过电位大且反应动力学差的情况下，严重阻碍了该技术的发展[6] [37]。因此很多研究都集中在碱性 OER 上，在已报道电催化剂中，LDH 尤其有希望用于 OER [13]。根据金属氢氧化物在碱性溶液中的传统 OER 机理，中间产物(MOH 和 MOOH)内部的成键相互作用(M-O)对整个 OER 活性至关重要[37] [38] [39]。氧原子与表面的相互作用越强，OH^-的吸附就越容易。因此，M-O 键强度被认为是 OER 催化活性的通用描述指标。此外，从分子轨道原理来看，OER 活性与过渡金属阳离子的 e_g 占据水平密切相。优秀的 OER 催化剂的表面阳离子 e_g 占有率应接近 1，以促进表面活性位点和吸附中间产物之间的电子转移[40] [41] [42]。因此，开发有效的策略来改变电子结并调整吸附剂与活性位点之间的相互作用是非常可取的。

氧空位工程是调整电催化剂电子结构有效方法，氧空位在 LDH 作为 OER 催化剂中的重要作用已被许多研究人员证实。Lang 等人认为氧空位的形成导致 NiFe-LDH 中 Ni 元素的价态从 Ni^{2+}转变为 Ni^{3+}，从而通过 Ni 和 Fe 位点之间的局部重构降低了电子转移势垒[43]。在这些理论的基础上，很对研究者致力于在 LDH 中引入氧空位来提高电催化性能，Wu 等人在水热过程中通过氮化碳(CN)中的吸电子基团层状双金属氢氧化物上产生氧空位。具有丰富氧空位 O_v-NiFe-LDH 具有优异的 OER 性能，在 10 mA cm^{-2} 时过电位仅为 214 mV [44]。Wang 等提出了一种简单的一锅合成法制备富缺陷异质结 CoNi-LDH 电催化剂，在 10 mA cm^{-2} 条件过电位为 257 mV，显示出卓越的 OER 性能。并通过密度泛函理计算表明，氧空位可以大大减小催化剂的带隙，使其具有优异的导电性[45]。Ding 等人通过简单的水热反应制备了一种新型的 Mo 掺杂 NiCo LDH，该材料具有丰富的氧空位，优异的稳定性和丰富的活性位点。密度泛函理论计证实，Mo 掺杂通过缺陷和氧空位的构建提供了新的活性位，在电流密度为 10 mA cm^{-2} 时，Mo-NiCo LDHs (Vo)表现出优异的电催化性能，OER 过电位为 258 mV，HER 过电位为 194 mV [25]。Liu 等人报道了一种简便的合成方法，采用简单的溶剂热法在乙醇-N,N-二甲基甲酰胺(DMF)混合溶液中进行，该溶液具有轻微的蚀刻效应，可获得三维开放结构。合成的 Ni_1Co_1-LDHs-E_1D_1 复合材料具有丰富的氧空位和大表面积的超薄纳米片形貌，这种分散良好的 3D 材料表面存在丰富的氧空位和反应位点，促进了电荷转移和传输，从而显著提高了 OER 性，这一项研究为在有机混合溶液中采用溶剂热法制备了稳定的富氧空位过

渡金属基 LDHs 电催化剂提供了启示[46]。更多的研究结果如表 1 所示。

Table 1. Electrocatalytic performance of LDH materials with various oxygen-containing vacancies
表 1. 各种含氧空位的 LDH 材料的电催化性能

材料	OER 过电位(mV)	HER 过电位(mV)	参考文献
Ov-NiFe-LDH	214 (η10)	/	[44]
CNT@NiCo-LDH-OV	257 (η10)	/	[45]
FeNiW-LDH	202 (η10)	/	[26]
P-Ru-CoFe LDH	275 (η10)	/	[32]
v-NiFe LDH	195 (η10)	/	[47]
IrO2@SL-NiFe LDHs	270 (η10)	/	[48]
Ni1Co1-LDHs-E1D1	260 (η10)	/	[46]
Mo-NiCo LDHs(Vo)	258 (η10)	194 (η10)	[25]
V-Ce/CoFe LDH	/	73 (η10)	[31]
v-NiFe LDH	/	87 (η10)	[49]

3.2. 富氧空位的 LDH 在超级电容器方面的应用

超级电容器因其高功率密度、快速充放电能力和更长的循环寿命而备受关注，作为电化学储能设备，其电容实现主要通过双电层电容和赝电容两种机制。与传统电池不同，超级电容器不受固态离子扩散的限制，能够快速存储和释放电荷[50]。尽管具有诸多优势，但超级电容器的能量密度相对较低，于是合理设计电极材料成为了解决问题的关键[51]。作为赝电容电极材料的代表，LDH 由于其相对较高的氧化还原活性、环境友好性和均匀分散的过渡金属原子的有效利用，它们被认为是有前途的电极材料[52] [53]。更重要的是，主体层阳离子中的易调性和阴离子在不改变结构的情况下的可交换性也赋予了它们有趣的电化学/电子特性[54]。然而相比于一些其他材料，LDH 的电化学性能可能不如人们期望的那样优越，特别是在导电性和循环稳定性方面。为了克服这些问题，氧缺陷引起了广泛的关注，因为其可以调节电极材料的电子特性，提供更多电化学活性位点[55] [56] [57]。因此，氧空位被广泛应用于制备高性能电极材料。在碱性电解液中，LDH 与氢氧根结合生成更高价的羟基氧化物，所以 OH^-在 LDH 表面的吸附行为是电极材料可逆电化学反应的另一个关键因素[58]，而大量研究表明氧空位的存在可以增强对 OH^-的吸附[9]。基于以上优点，大量研究者们在 LDH 中引入氧空位以提高其储能性能，Tang 等人第一次通过温和的 H_2O_2 处理 NiMn-LDH 来引入氧空位，显著提高了电化学储能性能，获得的 Ov-LDH 纳米片具有特殊的层次结构和更大的离子接触面积。通过氧化处理引起的氧空位提高了 Ov-LDH 复合材料倍率性能，并通过计算证实了 NiMn-LDH 对 OH^-几乎没有吸附能力，因为阴离子倾向于与表面羟基上的 H 原子结合。而丰富的氧空位提供不饱和配位镍原子作为吸附位点，大大降低了 LDH 对于 OH^-的吸附能，增强了传质动力学[34]。Zhou 等人通过镁粉作为自掺杂和还原剂在 CoNi-LDH 中引入氧空位，镁的轻度还原可以显著提高 CoNiMg-LDH 中氧空位的浓度，通过计算证实了适量的镁对于氧空位的生成具有促进作用，而丰富的氧空位可以增加活性位点，加速电子的传输，提高材料的导电性和增强对电解质的吸附能力[59]；Zhang 等人提出了一种水热合成引入氧空位策略，将含有 Co^{2+}和 Ga^{3+}的水溶液快速倒入六亚甲基四胺的水溶液中，然后进行温和快速的水热反应。这种温和快速的合成策略在超薄 LDH 纳米片中引入了大量的孔隙，导致 Co-Ga-LDH 中存在高浓度的氧空位，并且 X 射线光电子能谱和 EPR 所证实氧空位的浓度可

以任意调节，氧空位和引入的 Ga 离子的协同作用增强了 LDH 纳米片对 OH^-的吸附，使 $Co_{0.50}$-$Ga_{0.50}$-LDH 具有优异的超级电容器应用性能[60]。更多的研究进展见表 2。

Table 2. Supercapacitor performance of LDH materials with various oxygen vacancies
表 2. 各种含氧空位的 LDH 材料的超级电容器性能

材料	比电容	参考文献
Ov-NiMn-LDH	1183 C g^{-1} at 1 A g^{-1}	[34]
CoNiMg-LDH	1095.2 C g^{-1} at 1 A g^{-1}	[59]
Vo-NiCo LDH	1563.1 F g^{-1} at 1 A g^{-1}	[35]
MoNiCo-LDH-0.05/CC	471.1 mA h g^{-1} at 1 A g^{-1}	[29]
Ov-NiCo-LDH	1160 C g^{-1} at 1 A g^{-1}	[61]
CoO@Ov-NiCo LDH	2264.2 F g^{-1} at 1 A g^{-1}	[55]
$Co_{0.50}$-$Ga_{0.50}$-LDH	0.47 C·cm^{-2} at mA·cm^{-2}	[60]
CoAl LDH	799.2 F g^{-1} at 1 A g^{-1}	[16]
Mn–Ni LDO-C	1478.1 C g^{-1} at 1 mA cm^{-2}	[62]
MoO_{3-x}@NCLDH	3.49 F cm^{-2} at 1 mA cm^{-2}	[63]
Ov-CuCoLDH	1392.4 F g^{-1} at 1 A g^{-1}	[64]

4. 结论与展望

由于特殊的层状结构、主体层金属离子的可调性和层间阴离子的可交换性使得 LDH 其在催化和储能应用中具有巨大的潜力，但其导电性差、易堆叠、高电流密度下反应动力学迟缓以及循环稳定性弱等问题限制了其进一步应用，在 LDH 中引入氧空位可以提其导电性，增加活性位点的数量和加快传质动力学。在这篇综述中，我们试图总结最近在 LDH 中引入氧空位以提高其催化和储能性能方面的进展，在 LDH 中引入氧空位后可以大大提升 LDH 的电催化性能，其原因是改善了电荷转移，同时显著促进氢氧根离子的吸附，并改变含氧中间物种的吸附自由能。另外，氧空位的存在可以增强对 OH^-的吸附，增加活性位点，加速电子的传输和提高材料的导电性，提升 LDH 的储能性能。因此，引入氧空位是提升 LDH 的催化和储能性能的一种可行方法。深入了解氧空位的作用以及 LDH 不同活性位点之间在电子传递和表面反应中的协同作用是非常具有挑战性和意义的。这些问题需要更多的研究来解决，并为优良电极的精确设计提供指导。

参考文献

[1] Sharma, V., Aman, M. and Omar, S. (2022) NiMn-Layered Double Hydroxide Porous Nanoarchitectures as a Bifunctional Material for Accelerated P-Nitrophenol Reduction and Freestanding Supercapacitor Electrodes. *ACS Applied Nano Materials*, **5**, 15651-15664. https://doi.org/10.1021/acsanm.2c03719

[2] Yue, Q., Sun, J., Chen, S., Zhou, Y., Li, H., Chen, Y., Zhang, R., Wei, G. and Kang, Y. (2020) Hierarchical Mesoporous MXene-NiCoP Electrocatalyst for Water-Splitting. *ACS Applied Materials & Interfaces*, **12**, 18570-18577. https://doi.org/10.1021/acsami.0c01303

[3] Han, J., Zhang, J., Wang, T., Xiong, Q., Wang, W., Cao, L. and Dong, B. (2019) Zn Doped FeCo Layered Double Hydroxide Nanoneedle Arrays with Partial Amorphous Phase for Efficient Oxygen Evolution Reaction. *ACS Sustainable Chemistry & Engineering*, **7**, 13105-13114. https://doi.org/10.1021/acssuschemeng.9b02297

[4] Xu, Z., Yeh, C.L., Chen, J.L., Lin, J.T., Ho, K.C. and Lin, R.Y.Y. (2022) Metal-Organic Framework-Derived 2D NiCoP Nanoflakes from Layered Double Hydroxide Nanosheets for Efficient Electrocatalytic Water Splitting at High

Current Densities. *ACS Sustainable Chemistry & Engineering*, **10**, 11577-11586. https://doi.org/10.1021/acssuschemeng.2c03250

[5] Senthil Raja, D., Chuah, X.F. and Lu, S.Y. (2018) *In Situ* Grown Bimetallic MOF-Based Composite as Highly Efficient Bifunctional Electrocatalyst for Overall Water Splitting with Ultrastability at High Current Densities. *Advanced Energy Materials*, **8**, Article ID: 1801065. https://doi.org/10.1002/aenm.201801065

[6] Wang, Y., Yan, D., El Hankari, S., Zou, Y. and Wang, S. (2018) Recent Progress on Layered Double Hydroxides and Their Derivatives for Electrocatalytic Water Splitting. *Advanced Science*, **5**, Article ID: 1800064. https://doi.org/10.1002/advs.201800064

[7] Cheng, J. and Wang, D. (2022) 2D Materials Modulating Layered Double Hydroxides for Electrocatalytic Water Splitting. *Chinese Journal of Catalysis*, **43**, 1380-1398. https://doi.org/10.1016/S1872-2067(21)63987-6

[8] Zhou, J.J., Ji, W., Xu, L., Yang, Y., Wang, W., Ding, H., Xu, X., Wang, W., Zhang, P., Hua, Z. and Chen, L. (2022) Controllable Transformation of CoNi-MOF-74 on Ni Foam into Hierarchical-Porous $Co(OH)_2$/$Ni(OH)_2$ Micro-Rods with Ultra-High Specific Surface Area for Energy Storage. *Chemical Engineering Journal*, **428**, Article ID: 132123. https://doi.org/10.1016/j.cej.2021.132123

[9] Wu, H., Zhang, X., Xue, J., Zhang, H., Yang, L. and Li, S. (2021) Engineering Active Sites on Hierarchical ZnNi Layered Double Hydroxide Architectures with Rich Zn Vacancies Boosting Battery-Type Supercapacitor Performances. *Electrochimica Acta*, **374**, Article ID: 137932. https://doi.org/10.1016/j.electacta.2021.137932

[10] Wu, Y., Liu, Q., Wang, J., Liu, X. and Zhang, X. (2023) Effectively Morphology-Controlled NiMn Layered Double Hydroxide Microflowers by Conductive Silver Nanowires for Supercapacitor Electrodes. *Electrochimica Acta*, **460**, Article ID: 142623. https://doi.org/10.1016/j.electacta.2023.142623

[11] Jing, C., Dong, B. and Zhang, Y. (2020) Chemical Modifications of Layered Double Hydroxides in the Supercapacitor. *Energy & Environmental Materials*, **3**, 346-379. https://doi.org/10.1002/eem2.12116

[12] Tomboc, G.M., Kim, J., Wang, Y., Son, Y., Li, J., Kim, J.Y. and Lee, K. (2021) Hybrid Layered Double Hydroxides as Multifunctional Nanomaterials for Overall Water Splitting and Supercapacitor Applications. *Journal of Materials Chemistry A*, **9**, 4528-4557. https://doi.org/10.1039/D0TA11606H

[13] Chala, S.A., Tsai, M.C., Su, W.N., Ibrahim, K.B., Thirumalraj, B., Chan, T.S., Lee, J.F., Dai, H. and Hwang, B.J. (2020) Hierarchical 3D Architectured Ag Nanowires Shelled with NiMn-Layered Double Hydroxide as an Efficient Bifunctional Oxygen Electrocatalyst. *ACS Nano*, **14**, 1770-1782. https://doi.org/10.1021/acsnano.9b07487

[14] Jiao, Z., Chen, Y., Du, M., Demir, M., Yan, F., Xia, W., Zhang, Y., Wang, C., Gu, M., Zhang, X. and Zou, J. (2023) 3D Hollow NiCo LDH Nanocages Anchored on 3D CoO Sea Urchin-Like Microspheres: A Novel 3D/3D Structure for Hybrid Supercapacitor Electrodes. *Journal of Colloid and Interface Science*, **633**, 723-736. https://doi.org/10.1016/j.jcis.2022.11.131

[15] Xu, L., Li, Y., Li, M., Yu, N., Wang, W., Wei, F., Qi, J., Sui, Y., Li, L. and Zhang, L. (2024) Mo-Doped NiCo-LDH Nanoflower Derived from ZIF-67 Nanosheet Arrays for High-Performance Supercapacitors. *Journal of Energy Storage*, **77**, Article ID: 109781. https://doi.org/10.1016/j.est.2023.109781

[16] Wang, G. and Jin, Z. (2021) Oxygen-Vacancy-Rich Cobalt-Aluminium Hydrotalcite Structures Served as High-Performance Supercapacitor Cathode. *Journal of Materials Chemistry C*, **9**, 620-632. https://doi.org/10.1039/D0TC03640D

[17] Zhu, Y., Tahini, H.A., Hu, Z., Chen, Z.G., Zhou, W., Komarek, A.C., Lin, Q., Lin, H.J., Chen, C.T., Zhong, Y., Fernández-Díaz, M.T., Smith, S.C., Wang, H., Liu, M. and Shao, Z. (2020) Boosting Oxygen Evolution Reaction by Creating Both Metal Ion and Lattice-Oxygen Active Sites in A Complex Oxide. *Advanced Materials*, **32**, Article ID: 1905025. https://doi.org/10.1002/adma.201905025

[18] Zhong, H., Gao, G., Wang, X., Wu, H., Shen, S., Zuo, W., Cai, G., Wei, G., Shi, Y., Fu, D., Jiang, C., Wang, L.W. and Ren, F. (2021) Ion Irradiation Inducing Oxygen Vacancy-Rich NiO/NiFe2O4 Heterostructure for Enhanced Electrocatalytic Water Splitting. *Small*, **17**, Article ID: 2103501. https://doi.org/10.1002/smll.202103501

[19] Zhang, Y., Zhang, J., Li, G., Leng, D., Wang, W., Gao, Y., Gao, J., Liang, Q., Lu, H. and Wang, C. (2019) Metal-Organic Framework-Derived Porous TiO2 Nanotablets with Sensitive and Selective Ethanol Sensing. *Journal of Materials Science*: *Materials in Electronics*, **30**, 17899-17906. https://doi.org/10.1007/s10854-019-02142-x

[20] Zubair, M., Kumar, P., Klingenhof, M., Subhash, B., Yuwono, J.A., Cheong, S., Yao, Y., Thomsen, L., Strasser, P., Tilley, R.D. and Bedford, N.M. (2023) Vacancy Promotion in Layered Double Hydroxide Electrocatalysts for Improved Oxygen Evolution Reaction Performance. *ACS Catalysis*, **13**, 4799-4810. https://doi.org/10.1021/acscatal.2c05863

[21] Liu, H., Zhao, D., Liu, Y., Tong, Y., Wu, X. and Shen, G. (2021) NiMoCo Layered Double Hydroxides for Electrocatalyst and Supercapacitor Electrode. *Science China Materials*, **64**, 581-591. https://doi.org/10.1007/s40843-020-1442-3

[22] Gao, X., Wang, P., Pan, Z., Claverie, J.P. and Wang, J. (2020) Recent Progress in Two-Dimensional Layered Double

Hydroxides and Their Derivatives for Supercapacitors. *ChemSusChem*, **13**, 1226-1254. https://doi.org/10.1002/cssc.201902753

[23] Yang, S., Liu, Y., Hao, Y., Yang, X., Goddard Iii, W.A., Zhang, X.L. and Cao, B. (2018) Oxygen-Vacancy Abundant Ultrafine Co3O4/Graphene Composites for High-Rate Supercapacitor Electrodes. *Advanced Science*, **5**, Article ID: 1700659. https://doi.org/10.1002/advs.201700659

[24] Ma, Q., Cui, F., Zhang, J., Qi, X. and Cui, T. (2022) Surface Engineering of Co3O4 Nanoribbons Forming Abundant Oxygen-Vacancy for Advanced Supercapacitor. *Applied Surface Science*, **578**, Article ID: 152001. https://doi.org/10.1016/j.apsusc.2021.152001

[25] Chen, K., Cao, Y.H., Yadav, S., Kim, G.C., Han, Z., Wang, W., Zhang, W.J., Dao, V. and Lee, I.H. (2023) Electronic Structure Reconfiguration of Nickel-Cobalt Layered Double Hydroxide Nanoflakes Via Engineered Heteroatom and Oxygen-Vacancies Defect for Efficient Electrochemical Water Splitting. *Chemical Engineering Journal*, **463**, Article ID: 142396. https://doi.org/10.1016/j.cej.2023.142396

[26] He, J., Zhou, X., Xu, P. and Sun, J. (2021) Promoting Electrocatalytic Water Oxidation through Tungsten-Modulated Oxygen Vacancies on Hierarchical FeNi-Layered Double Hydroxide. *Nano Energy*, **80**, Article ID: 105540. https://doi.org/10.1016/j.nanoen.2020.105540

[27] Li, C., Li, X.J., Zhao, Z.Y., Li, F.L., Xue, J.Y., Niu, Z., Gu, H.W., Braunstein, P. and Lang, J.P. (2020) Iron-Doped NiCo-MOF Hollow Nanospheres for Enhanced Electrocatalytic Oxygen Evolution. *Nanoscale*, **12**, 14004-14010. https://doi.org/10.1039/D0NR01218A

[28] Chen, L., Zhang, Y., Li, D., Wang, Y. and Duan, C. (2018) Magnesium-Regulated Oxygen Vacancies of Nickel Layered Double Hydroxides for Electrocatalytic Water Oxidation. *Journal of Materials Chemistry A*, **6**, 18378-18383. https://doi.org/10.1039/C8TA04615H

[29] Ding, Y., Yan, Z., Wang, G., Sang, H., Xu, Z. and Li, W. (2024) Regulating The Oxygen Vacancy and Electronic Structure of NiCo Layered Double Hydroxides by Molybdenum Doping for High-Power Hybrid Supercapacitors. *Small*, **20**, Article ID: 2306382. https://doi.org/10.1002/smll.202306382

[30] Liu, Y., Zhang, M., Hu, D., Li, R., Hu, K. and Yan, K. (2019) Ar Plasma-Exfoliated Ultrathin NiCo-Layered Double Hydroxide Nanosheets for Enhanced Oxygen Evolution. *ACS Applied Energy Materials*, **2**, 1162-1168. https://doi.org/10.1021/acsaem.8b01717

[31] Liu, S., Zhu, J., Sun, M., Ma, Z., Hu, K., Nakajima, T., Liu, X., Schmuki, P. and Wang, L. (2020) Promoting the Hydrogen Evolution Reaction through Oxygen Vacancies and Phase Transformation Engineering on Layered Double Hydroxide Nanosheets. *Journal of Materials Chemistry A*, **8**, 2490-2497. https://doi.org/10.1039/C9TA12768B

[32] Li, J., Shi, J., Hu, Y., Li, M. and Kang, Y. (2024) Plasma-Induced Vacancy Defects of Ru-Doped CoFe Layered Double Hydroxide for Superior Oxygen Evolution Activity. *Journal of Alloys and Compounds*, **976**, Article ID: 173076. https://doi.org/10.1016/j.jallcom.2023.173076

[33] Tang, Y., Liu, Q., Dong, L., Wu, H.B. and Yu, X.Y. (2020) Activating the Hydrogen Evolution and Overall Water Splitting Performance of NiFe LDH by Cation Doping and Plasma Reduction. *Applied Catalysis B*: *Environmental*, **266**, Article ID: 118627. https://doi.org/10.1016/j.apcatb.2020.118627

[34] Tang, Y., Shen, H., Cheng, J., Liang, Z., Qu, C., Tabassum, H. and Zou, R. (2020) Fabrication of Oxygen-Vacancy Abundant NiMn-Layered Double Hydroxides for Ultrahigh Capacity Supercapacitors. *Advanced Functional Materials*, **30**, Article ID: 1908223. https://doi.org/10.1002/adfm.201908223

[35] Liang, H., Jia, H., Lin, T., Wang, Z., Li, C., Chen, S., Qi, J., Cao, J., Fei, W. and Feng, J. (2019) Oxygen-Vacancy-Rich Nickel-Cobalt Layered Double Hydroxide Electrode for High-Performance Supercapacitors. *Journal of Colloid and Interface Science*, **554**, 59-65. https://doi.org/10.1016/j.jcis.2019.06.095

[36] Chen, X., Zhang, Y., Yang, J., Xiao, J.D., Yang, Z. and Wang, J. (2023) Boosting Oxygen Evolution Performance of Nickel-Iron Layered Double Hydroxides by Controlling Oxygen Vacancies and Structural Disorder *via* N-Butyllithium Treatment. *Inorganic Chemistry*, **62**, 19795-19803. https://doi.org/10.1021/acs.inorgchem.3c03457

[37] Zhu, K., Wu, T., Li, M., Lu, R., Zhu, X. and Yang, W. (2017) Perovskites Decorated with Oxygen Vacancies and Fe-Ni Alloy Nanoparticles as High-Efficiency Electrocatalysts for the Oxygen Evolution Reaction. *Journal of Materials Chemistry A*, **5**, 19836-19845. https://doi.org/10.1039/C7TA05404A

[38] GarcÍA-Mota, M., Bajdich, M., Viswanathan, V., Vojvodic, A., Bell, A.T. and Nørskov, J.K. (2012) Importance of Correlation in Determining Electrocatalytic Oxygen Evolution Activity on Cobalt Oxides. *The Journal of Physical Chemistry C*, **116**, 21077-21082. https://doi.org/10.1021/jp306303y

[39] Suntivich, J., May, K.J., Gasteiger, H.A., Goodenough, J.B. and Shao-Horn, Y. (2011) A Perovskite Oxide Optimized for Oxygen Evolution Catalysis from Molecular Orbital Principles. *Science*, **334**, 1383-1385. https://doi.org/10.1126/science.1212858

[40] Man, I.C., Su, H.Y., Calle-Vallejo, F., Hansen, H.A., MartÍNez, J.I., Inoglu, N.G., Kitchin, J., Jaramillo, T.F., Nørskov,

J.K. and Rossmeisl, J. (2011) Universality in Oxygen Evolution Electrocatalysis on Oxide Surfaces. *ChemCatChem*, **3**, 1159-1165. https://doi.org/10.1002/cctc.201000397

[41] Lee, S., Nam, G., Sun, J., Lee, J.S., Lee, H.W., Chen, W., Cho, J. and Cui, Y. (2016) Enhanced Intrinsic Catalytic Activity of λ-MnO_2 by Electrochemical Tuning and Oxygen Vacancy Generation. *Angewandte Chemie International Edition*, **55**, 8599-8604. https://doi.org/10.1002/anie.201602851

[42] Guo, Y., Tong, Y., Chen, P., Xu, K., Zhao, J., Lin, Y., Chu, W., Peng, Z., Wu, C. and Xie, Y. (2015) Engineering The Electronic State of a Perovskite Electrocatalyst for Synergistically Enhanced Oxygen Evolution Reaction. *Advanced Materials*, **27**, 5989-5994. https://doi.org/10.1002/adma.201502024

[43] Zhao, Z., Shao, Q., Xue, J., Huang, B., Niu, Z., Gu, H., Huang, X. and Lang, J. (2022) Multiple Structural Defects in Ultrathin NiFe-LDH Nanosheets Synergistically and Remarkably Boost Water Oxidation Reaction. *Nano Research*, **15**, 310-316. https://doi.org/10.1007/s12274-021-3475-z

[44] Wu, K., Shi, L., Wang, Z., Zhu, Y., Tong, X., He, W., Wang, J., Zheng, L., Kang, Y., Shan, W., Wang, Z., Huang, A. and Jiang, B. (2023) A General Strategy to Generate Oxygen Vacancies in Bimetallic Layered Double Hydroxides for Water Oxidation. *Chemical Communications*, **59**, 3138-3141. https://doi.org/10.1039/D3CC00096F

[45] Wang, H., Yuan, Y., Gu, J., Jia, Z. Lu, Z., Bai, Z., Yang, L. and Yang, X. (2020) Facile One-Pot Synthesis of Layered Double Hydroxides Nanosheets with Oxyge N Vacancies Grown on Carbon Nanotubes for Efficient Oxygen Evolution Reaction. *Journal of Power Sources*, **467**, Article ID: 228354. https://doi.org/10.1016/j.jpowsour.2020.228354

[46] Liu, Y., Chen, Y., Ge, R., Li, W., Zhang, Y., Feng, L. and Che, R. (2020) 3D Freestanding Flower-Like Nickel-Cobalt Layered Double Hydroxides Enriched with Oxygen Vacancies as Efficient Electrocatalysts for Water Oxidation. *Sustainable Materials and Technologies*, **25**, e00170. https://doi.org/10.1016/j.susmat.2020.e00170

[47] Liu, S., Zhang, H., Hu, E., Zhu, T., Zhou, C., Huang, Y., Ling, M., Gao, X. and Lin, Z. (2021) Boosting Oxygen Evolution Activity of NiFe-LDH Using Oxygen Vacancies and Morphological Engineering. *Journal of Materials Chemistry A*, **9**, 23697-23702. https://doi.org/10.1039/D1TA06263H

[48] Li, D., Li, T., Hao, G., Guo, W., Chen, S., Liu, G., Li, J. and Zhao, Q. (2020) IrO2 Nanoparticle-Decorated Single-Layer NiFe LDHs Nanosheets with Oxygen Vacancies for the Oxygen Evolution Reaction. *Chemical Engineering Journal*, **399**, Article ID: 125738. https://doi.org/10.1016/j.cej.2020.125738

[49] Yuan, Z., Bak, S.M., Li, P., Jia, Y., Zheng, L., Zhou, Y., Bai, L., Hu, E., Yang, X.Q., Cai, Z., Sun, Y. and Sun, X. (2019) Activating Layered Double Hydroxide with Multivacancies by Memory Effect for Energy-Efficient Hydrogen Production at Neutral PH. *ACS Energy Letters*, **4**, 1412-1418. https://doi.org/10.1021/acsenergylett.9b00867

[50] Ding, Q., Yin, J., Huang, Y., Wang, C., Luo, H., Sun, S., Xu, Y. and Li, H. (2024) Construction of Porous Flower-Like Ru-Doped CoNiFe Layered Double Hydroxide for Supercapacitors and Oxygen Evolution Reaction Catalysts. *Journal of Colloid and Interface Science*, **664**, 263-274. https://doi.org/10.1016/j.jcis.2024.03.044

[51] Lin, Z., Li, X., Zhang, H., Xu, B.B., Wasnik, P., Li, H., Singh, M.V., Ma, Y., Li, T. and Guo, Z. (2023) Research Progress of MXenes and Layered Double Hydroxides for Supercapacitors. *Inorganic Chemistry Frontiers*, **10**, 4358-4392. https://doi.org/10.1039/D3QI00819C

[52] Jiang, H., Ke, Q., Qiu, X., Chen, J., Chen, P., Wang, S., Luo, X. and Rao, B. (2023) NiCo Layered Double Hydroxide Nanocages for High-Performance Asymmetric Supercapacitors. *Inorganic Chemistry Frontiers*, **10**, 2154-2164. https://doi.org/10.1039/D2QI02763A

[53] Wang, L. and Chen, X. (2022) NiCo Layered Double Hydroxide on Three-Dimensional Modified Graphite Paper for High-Performance Supercapacitors. *Journal of Alloys and Compounds*, **907**, Article ID: 164411. https://doi.org/10.1016/j.jallcom.2022.164411

[54] Spahr, M.E., Novák, P., Schnyder, B., Haas, O. and Nesper, R. (1998) Characterization of Layered Lithium Nickel Manganese Oxides Synthesized by a Novel Oxidative Coprecipitation Method and Their Electrochemical Performance as Lithium Insertion Electrode Materials. *Journal of the Electrochemical Society*, **145**, 1113. https://doi.org/10.1149/1.1838425

[55] Cao, X.M., Liu, D., Sun, Z.J. and Zhang, Q. (2024) *In Situ* Construction of Core-Shell Structured Cobalt Oxide@Nickel-Cobalt-Layered Double Hydroxide Nanorods with Abundant Oxygen Vacancies towards Boosting Electrochemical Energy Storage. *Inorganic Chemistry Frontiers*, **11**, 789-798. https://doi.org/10.1039/D3QI02214E

[56] Zhai, T., Xie, S., Yu, M., Fang, P., Liang, C., Lu, X. and Tong, Y. (2014) Oxygen Vacancies Enhancing Capacitive Properties of MnO2 Nanorods for Wearable Asymmetric Supercapacitors. *Nano Energy*, **8**, 255-263. https://doi.org/10.1016/j.nanoen.2014.06.013

[57] Khazaee, Z., Mahjoub, A.R., Khavar, A.H.C., Srivastava, V. and Sillanpää, M. (2020) Preparation of Phosphorus-Modified BiO_x as Versatile Catalyst for Enhanced Photo-Reduction of Cr(VI) and Oxidation of Organic Dyes. *Solar Energy*, **207**, 1282-1299. https://doi.org/10.1016/j.solener.2020.07.068

[58] Li, J., Liu, Z., Zhang, Q., Cheng, Y., Zhao, B., Dai, S., Wu, H.H., Zhang, K., Ding, D., Wu, Y., Liu, M. and Wang,

M.S. (2019) Anion and Cation Substitution in Transition-Metal Oxides Nanosheets for High-Performance Hybrid Supercapacitors. *Nano Energy*, **57**, 22-33. https://doi.org/10.1016/j.nanoen.2018.12.011

[59] Zhou, G., Gao, X., Wen, S., Wu, X., Zhang, L., Wang, T., Zhao, P., Yin, J. and Zhu, W. (2022) Magnesium-Regulated Oxygen Vacancies of Cobalt-Nickel Layered Double Hydroxide Nanosheets for Ultrahigh Performance Asymmetric Supercapacitors. *Journal of Colloid and Interface Science*, **612**, 772-781. https://doi.org/10.1016/j.jcis.2021.12.087

[60] Zhang, H., Bai, Y., Chen, H., Wu, J., Li, C.M., Su, X. and Zhang, L. (2022) Oxygen-Defect-Rich 3D Porous Cobalt-Gallium Layered Double Hydroxide for High-Performance Supercapacitor Application. *Journal of Colloid and Interface Science*, **608**, 1837-1845. https://doi.org/10.1016/j.jcis.2021.10.109

[61] Wang, T., Liu, K., Gao, Z., Zeng, Z., Mao, R., Zhu, G., Ni, J., Xu, X., Jia, R. and Han, S. (2022) Oxygen Vacancy-Rich Flower-Like Nickel Cobalt Layered Double Hydroxides for Supercapacitors with Ultrahigh Capacity. *Ceramics International*, **48**, 19798-19805. https://doi.org/10.1016/j.ceramint.2022.03.254

[62] Jiang, S., Qiao, Y., Fu, T., Peng, W., Yu, T., Yang, B., Xia, R. and Gao, M. (2021) Integrated Battery-Capacitor Electrodes: Pyridinic N-Doped Porous Carbon-Coated Abundant Oxygen Vacancy Mn-Ni-Layered Double Oxide for Hybrid Supercapacitors. *ACS Applied Materials & Interfaces*, **13**, 34374-34384. https://doi.org/10.1021/acsami.1c08699

[63] Zhang, H., Lv, Y., Wu, X., Guo, J. and Jia, D. (2022) Electrodeposition Synthesis of High Performance MoO_{3-X}@Ni-Co Layered Double Hydroxide Hierarchical Nanorod Arrays for Flexible Solid-State Supercapacitors. *Chemical Engineering Journal*, **431**, Article ID: 133233. https://doi.org/10.1016/j.cej.2021.133233

[64] Xu, X., Lu, H., Xu, D., Zhou, P., Ying, Y., Li, L. and Liu, Y. (2023) Oxygen-Rich Vacancies CuCoLDH with 1D/2D Nanoarray Structure for High Performance Asymmetric Supercapacitor. *Applied Surface Science*, **614**, Article ID: 156174. https://doi.org/10.1016/j.apsusc.2022.156174