

Supplementary Information

# Recent Advances in Nanoscale Based Electrocatalysts for Metal-Air Battery, Fuel Cell and Water-Splitting Applications: An Overview

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**Citation:** Chen, T.-W.; Anushya, G.; Chen, S.-M.; Kalimuthu, P.; Mariyappan, V.; Gajendran, P.; Ramachandran, R. Recent Advances in Nanoscale Based Electrocatalysts for Metal-Air Battery, Fuel Cell and Water-Splitting Applications; An Overview. *Materials* **2022**, *15*, 458. <https://doi.org/10.3390/ma15020458>

Academic Editors: Vincenzo Baglio and Carmelo Lo Vecchio

Received: 27 October 2021

Accepted: 4 January 2022

Published: 8 January 2022

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**Table S1.** Comparison of fuel cell performances on various electrocatalysts.

Synthesis Route	Catalysts	Overpotential/Onset potential (mV)	Current Density (mA cm <sup>-2</sup> )	Medium (M)	Ref.
Sol-gel	Pt/Clay/Nafion	910	4.2	05 H <sub>2</sub> SO <sub>4</sub>	[1]
Solvothermal	PVA/SGO/Fe <sub>3</sub> O <sub>4</sub>	670	25.57	1M NaCl	[2]
Hummer's	Fe/Ni-MOFs/NG-20	109	8.56	0.1 KOH	[3]
Calcinations	Hematite-LCP electrolyte	940	-	LaCePrO <sub>x</sub> (LCP)	[4]
CVD	Pt/GC-240	940	661	Polyelectrolyte	[5]
	Pt/GC-500	940	653		
Hydrothermal	Pt/TiO <sub>2</sub> /rGO	750	45.8	05 H <sub>2</sub> SO <sub>4</sub>	[6]
Hummer's	Pt-MnO <sub>2</sub> -ERGO	360	1.76	01 H <sub>2</sub> SO <sub>4</sub>	[7]
Hummer's	XC-72/Carbon/Pd	550	7.3	05 H <sub>2</sub> SO <sub>4</sub>	[8]
Electrodeposition	Co <sub>3</sub> O <sub>4</sub> -3DrGO/Nif	442	0.012	0.1 KOH	[9]
Solution casting	SPEEK/PABS-SWCNT	660	80	05 H <sub>2</sub> SO <sub>4</sub>	[10]

**Table S2.** Summary of ORR and OER electrocatalytic activities of the reported various types of advanced nanoscale based catalysts.

Synthesis Route	Catalysts	Morphology	Specific Capacity (mAh g <sup>-1</sup> )	Current Density (mA cm <sup>-2</sup> )	Medium (M)	Ref.
Electrospinning	Fe <sub>3</sub> C@N-CFs	Nanofiber	1287.3	10	0.1 KOH	[11]
Coating	Co <sup>II</sup> -salen/MWCNT@MnO <sub>2</sub>	Nanosheet	1000	0.15	-	[12]
Electrodeposition	Co <sub>3</sub> O <sub>4</sub> @Co/NCNT	Core-shell	891	135	0.5 H <sub>2</sub> SO <sub>4</sub>	[13]
Hydrothermal	Zn-Co-SNN/CFP	Nanoplate	484.7	10	0.1 KOH	[14]
Hydrothermal	NP Co <sub>3</sub> O <sub>4</sub> /Fe@C <sub>2</sub> N	Nanoparticles	790.1	165.8	0.1 KOH	[15]
Hydrothermal	800N,P-CNT	Porous structure	762	20	0.1 KOH	[16]
Solid-state	PANI@ZnPC	Pores structure	713	-	7 KOH	[17]
Dissolution	PVA-5wt.%SiO <sub>2</sub> GPE	Porous structure	720.6	0.3	0.1 KOH	[18]
Hydrothermal	8-MnO <sub>2</sub> /N-rGO	Wrinkled structure	5250	0.2	0.1 KOH	[19]
Solution combustion	Co/CoFe <sub>2</sub> O <sub>4</sub>	Porous structure	4320	100	0.1 KOH	[20]

## References

- Qin, X.; Huang, Y.; Wang, K.; Xu, T.; Wang, Y.; Wang, M.; Zhao, M.; Gao, Q. High efficient oxygen reduction reaction catalyst derived from Fe/Ni-mixed metal-organic frame works for application of fuel cell cathode. *Ind. Eng. Chem. Res.* **2019**, *58*, 10224–10237.
- Narayanamoorthy, B.; Datta, K.K.R.; Eswaramoorthy, M.; Balaji, S. Improved Oxygen Reduction Reaction Catalyzed by Pt/Clay/Nafion Nanocomposite for PEM Fuel Cells. *ACS Appl. Mater. Interfaces* **2012**, *4*, 3620–3626, doi:10.1021/am300697q.
- Beydaghi, H.; Javankakht, M. Aligned nanocomposite membrane containing sulfonated graphene oxide with superior ionic conductivity for direct methanol fuel cell applications. *Ind. Eng. Chem. Res.* **2015**, *54*, 7028–7037.
- Xia, C.; Cai, Y.; Ma, Y.; Wang, B.; Zhang, W.; Karlsson, M.; Wu, Y.; Zhu, B. Natural Mineral-Based Solid Oxide Fuel Cell with Heterogeneous Nanocomposite Derived from Hematite and Rare-Earth Minerals. *ACS Appl. Mater. Interfaces* **2016**, *8*, 20748–20755, doi:10.1021/acsami.6b05694.
- Ramaprabhu, S.; Aravind, S.S.J. Pt-nanoparticle-dispersed graphene-wrapped MWCNT composites as oxygen reduction electrocatalyst in proton exchange membrane fuel cell. *ACS Appl. Mater. Interfaces* **2012**, *4*, 3805–3810.
- Xia, B.Y.; Wu, H.B.; Chen, J.S.; Wang, Z.; Wang, X.; Lou, X.W. Formation of Pt-TiO<sub>2</sub>-rGO<sub>3</sub>-phase junction with significantly enhanced electro-activity for methanol oxidation. *Phys. Chem. Chem. Phys.* **2012**, *14*, 473–476.
- Ezhilvilian, A.T.; Rajkumar, M.; Chen, S.M.; Hu, C.C.; Boopathi, K.M.; Chu, C.W. Highly electrocatalytic performance of platinum and manganese dioxide nanoparticle decorated reduced graphene oxide sheets for methanol electro-oxidation. *RSC Adv.* **2014**, *4*, 41387–41397.
- Huang, H.; Wang, X. Pd nanoparticles supported on low-defect graphene sheets: for use as high-performance electrocatalysts for formic acid and methanol oxidation. *J. Mater. Chem.* **2012**, *22*, 22533–22541, doi:10.1039/c2jm33727d.
- Sundaradev, R.; Purkait, T. Fabrication of a membraneless non-enzymatic glucose-air fuel cell with graphene-cobalt oxide nanocomposite anode and Fe, N-doped biomass carbon cathode. *J. Electroanal. Chem.* **2020**, *874*, 114467.
- Shukla, A.; Dhanasekaran, P.; Sasikala, S.; Nagaraju, N.; Bhat, S.D.; Pillai, V.K. Nanocomposite membrane electrolyte of polyamino benzene sulfonic acid grafted single walled carbon nanotubes with sulfonated polyether ketone for direct methanol fuel cells. *Int. J. Hydrogen Energy* **2019**, *44*, 27564–27574, doi:10.1016/j.ijhydene.2019.08.189.
- Ma, Y.; Sumboja, A.; Zhang, W.; Yin, S.; Wang, S.X.; Pennycook, S.J.; Kou, Z.; Li, X.; Wang, J. Flexible and warable all-solid-state Al-air battery based on iron carbide encapsulated in electrospun porous carbon nanofibers. *ACS Appl. Mater. Interfaces* **2019**, *11*, 1988–1995.
- Hu, X.; Wang, J.; Li, X.; Wang, J.; Gregory, D.H.; Chen, J. MWCNT@MnO<sub>2</sub> nanocomposite cathode integrated with soluble O-carrier Co-salen in electrolyte for high-performance Li-Air batteries. *Nano Lett.* **2017**, *17*, 2073–2078.
- Sing, T.; Das, C.; Bothra, N.; Sikdar, N.; Das, S.; Pati, S.K.; Maji, T.K. MOF derived Co<sub>3</sub>O<sub>4</sub>/Co/NCNT nanocomposite for electrochemical hydrogen evolution, flexible Zinc-air batteries and overall water splitting. *Inorg. Chem.* **2020**, *5*, 3160–3170.
- Wu, X.; Han, X.; Ma, X.; Zhang, W.; Deng, Y.; Zhong, C.; Hu, W. Morphology-controllable synthesis of Zn-Co mixed sulfide

- nanostructures on carbon fiber paper towards efficient rechargeable Zinc-air batteries and water electrolysis. *ACS Appl. Mater. Interfaces* **2017**, *9*, 12574–12583.
15. Kim, J.; Gwon, O.; Mahmood, J.; Kim, C.; Yang, Y.; Lee, H.; Lee, J.H.; Jeong, H.Y.; Baek, J.B.; Kim, G. Synergetic coupling derived cobalt oxide with nitrogenated holly two-dimensional matrix as an efficient bifunctional catalyst for metal-air batteries. *ACS Nano*. **2019**, *5*, 5502–5512.
  16. Li, Z.; Zhao, W.; Yin, C.; Wei, L.; Wu, W.; Hu, Z.; Wu, M.; Synergistic effects between doped nitrogen and phosphorous in metal-free cathode for Zinc-air battery from covalent organic frameworks coated CNT. *ACS Appl. Mater. Interfaces* **2017**, *9*, 44519–44528.
  17. Deyab, M.; Mele, G.; Protected], [Email Polyaniline/Zn-phthalocyanines nanocomposite for protecting zinc electrode in Zn-air battery. *J. Power Sources* **2019**, *443*, 227264, doi:10.1016/j.jpowsour.2019.227264.
  18. Fan, X.; Liu, J.; Song, Z.; Han, X.; Deng, Y.; Zhong, C.; Hu, W. Porous nanocomposite gel polymer electrolyte with high ionic conductivity and superior electrolytic retention capacity for long-cycle life flexible Zinc-air batteries. *Nano Energy*, *56*, 454–462.
  19. Zhoor, A.; Faizan, R.; Elsaid, K.; Hashmi, S.; Butt, F.A.; Ghouri, Z.H. Synthesis and experimental investigation of  $\delta$ -MnO<sub>2</sub>/N-rGO nanocomposite for Li-O<sub>2</sub> batteries applications. *Chem. Eng. J. Adv.* **2021**, *7*, 100115.
  20. Athika, M.; Elumalai, P. Co/CoFe<sub>2</sub>O<sub>4</sub> decorated porous carbon network as air-breathing electrode for high-capacity rechargeable lithium-air battery; Role of Metallic Co nanoparticle. *Chem. Electro. Chem.* **2020**, *7*, 4188–4200.