Electronic Supplementary Material (ESI) for Chemical Society Reviews.

Supplementary Information

Nanoscale engineering of solid-state materials for boosting hydrogen storage

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Table S1. Comparison of different hydrogen storage technologies.

Storage method	Conditions	Equipment/Materials	Hydrogen storage capacity	Advantages	Disadvantages	Ref.
Compressed hydrogen storage	200~700 bar room temperature	Type I: pressure cylinder all made with metal Type II: pressure vessel made of metal liner with hoop wrapping Type III: pressure vessel made of metal liner with full composite wrapping Type IV: pressure vessel made of plastic liner with full composite wrapping	11.0 kg/m^3 (200 bar) 39.0 kg/m^3 (700 bar)	· Technical simplicity and reliability · Fast filling-releasing rate · Commercially available	· Safety issue at higher storage pressure · Relatively low volumetric storage density · High compression energy · Require heat management during charging · High transport costs · Heavy and expensive high-pressure tanks	1-3
Liquid hydrogen storage	1 bar <-253 ^{o}C	Cryogenic storage tanks (double walled and vacuum insulated)	70.8 kg/m^3 Size dependent	· High gravimetric density (>5.00 wt.%) · Commercially available	· H_2 loss · Safety issue at super low temperatures · High liquefaction energy · Heat management to reduce · Low boiling point of liquid hydrogen · Require specialized and expensive equipment	1-4
Cryo-compressed hydrogen storage	250~350 bar <-253 ^{o}C	Type III pressure vessel consists of aluminum liner wrapped with carbon fiber composite	87.0 kg/m^3	· High volumetric capacity · Rapid filling-releasing rate	· High pressure · High compression/liquefaction energy · Safety issue at high pressure and super low temperature · More expensive storage vessel	2, 3, 5
Liquid organic hydrogen carriers	30~50 bar 150~200 ^{o}C with catalysts	Toluene/Methylcyclohexane; Dibenzyltoluene/Perhydro-dibenzytoluene	47.7 kg/m^3, 6.16 wt.% 57.0 kg/m^3, 6.20 wt.%	· High hydrogen storage capacity · Closed carbon cycle · Long-cycle storage and transport	· High energy consumption for dehydrogenation · Difficulty in developing dehydrogenation catalysts · Short cycle life	1, 6
Adsorbed hydrogen in porous materials	1~100 bar -196 ^{o}C or room temperature	Porous carbons (Activated carbon, Carbon nanotubes, Graphene, biomass-derived carbon, MOF-derived carbon, etc.) Metal-organic frameworks Covalent organic frameworks	1.00~12.00 wt.% 1.00~18.00 wt.% 1.00~12.00 wt.%	· Light weight · Fast charging–discharging speed · Fully reversible · High security performance	· Easily influenced by reaction conditions and material preparation processes · Low room temperature capacity	1, 2
Absorbed hydrogen in metal/complex hydrides	1 bar >100 ^{o}C	Elemental hydrides (MgH_2) Intermetallic hydrides ($LaNi_5$, FeTi, Zr-based, Ti-based, Mg_2Ni, etc.) Complex hydrides ($NaAlH_4$, $LiAlH_4$, $Mg(AlH_4)_2$, $NaBH_4$, $LiBH_4$, $Mg(BH_4)_2$, $LiNH_2$, etc.)	7.65 wt.% 1.00~8.00 wt.% 7.40~18.80 wt.%	· High volumetric density · Fully reversible · High security performance	· Low sorption and desorption kinetics · High hydrogen release temperature · Formation of undesirable gases during discharging the hydrogen · Limited gravimetric capacity	1, 2, 7
Absorbed hydrogen in chemical hydrides	>100 ^{o}C	Ammonia borane (NH_3BH_3) Hydrazine borane ($N_2H_4BH_3$) Hydrous hydrazine (H_2NNH_2), etc.	19.60 wt.% 15.40 wt.% 12.50 wt.%	· Good gravimetric/volumetric capacity	· High hydrogen release temperature · No on-board regeneration · Require thermal management · Undesirable gaseous by-products	2, 8, 9

Table S2. Overview of recent reviews on the topic of hydrogen storage and the difference between our review and previously reported ones.

Title	Ref.	Year	Porous materials	Metal hydrides	Insights on nanomaterials	Nanoscale tuning and designing	DOI
Hydrogen storage in metal-organic frameworks	10	2012	√ (MOFs)	-	-	-	10.1021/cr200274s
Energy storage applications of activated carbons: supercapacitors and hydrogen storage	11	2014	√ (Carbons)	-	-	-	10.1039/C3EE43525C
Hydrogen storage in Mg: A most promising material	12	2010	-	√ (Mg hydrides)	-	-	10.1016/j.ijhydene.2009.08.088
High capacity hydrogen storage materials: attributes for automotive applications and techniques for materials discovery	13	2010	√	√	-	-	10.1039/B802882F
Hydrogen energy, economy and storage: Review and recommendation	14	2019	-	√	-	-	10.1016/j.ijhydene.2019.04.068
A review on the current progress of metal hydrides material for solid-state hydrogen storage applications	15	2016	-	√	-	-	10.1016/j.ijhydene.2016.05.244
Dimensional effects of nanostructured Mg/MgH_2 for hydrogen storage applications: A review	16	2017	-	√ (Mg/MgH_2)	√	-	10.1016/j.rser.2017.01.107
Recent advances and remaining challenges of nanostructured materials for hydrogen storage applications	17	2017	√	√	√	-	10.1016/j.pmatsci.2017.03.001
Nanostructured metal hydrides for hydrogen storage	18	2018	-	√	√ (Metal hydrides)	√ (Metal hydrides)	10.1021/acs.chemrev.8b00313
Perspectives and challenges of hydrogen storage in solid-state hydrides	19	2021	-	√	-	-	10.1016/j.cjche.2020.08.024
Nanoscale engineering of solid-state materials for boosting hydrogen storage	Our review	2023	√	√	√	√	

Table S3. References for hydrogen storage materials in Figs. 3, 5, and 10.

Materials	Ref.	Materials	Ref.	Materials	Ref.	Materials	Ref.
Superactivated carbide-derived carbon	20	Heteroatom self-doped activated biocarbon	21	Bamboo-based AC	22	Posidonia Oceanica-derived AC	23
Cigarette butts derived porous carbon	24	Oxygen-rich microporous carbon	25	Few-layer graphene-like flakes	26	Nitrogen-doped porous carbons	27
Coffee bean waste-derived AC	28	Sword-bean shells-derived AC	21	ZTC	29	Activated carbon cloth	30
Activated CNTs	31	Coffee waste-derived nanoporous carbons	32	Activated ZTC	29	Nanoporous activated carbon cloth	33
Activated rGO	34	Olive pomace AC	35	Cu-MOF-74	36	HKUST	36
NOTT-112	36	NU-125	36	rht-MOF-7	36	PCN-250	36
NU-1000	36	UiO-67	36	UiO-68-Ant	36	CYCU-3-Al	36
MFU-4*l*-Li	37	MFU-4*l*	37, 38	MOF-5	39, 40	NU-1501-Al	41
NU-1501-Fe	41	NU-1500-Al	41	NU-1102	42	NU-1103	42, 43
NU-1101	42	IRMOF-20	40	BUT-22	44	SNU-70	45
UMCM-9	45	PCN-610/NU-100	45	UiO-66	46	Fe-BTT	47
MIL-100(Fe)	48, 49	MOF-177	48, 49	ZIF-8	48, 49	MOF-210	50, 51
COF-1	52, 53	COF-5	52, 53	COF-102	54, 55	COF-103	54, 55
BP-COF-5	56	N-HEG	57	N-SG	58	P-doped GO	59
BCNT	60	Pd-MWCNTs	61	Pd/N-SG	58	Pt-CAs	62
Pt-HEG	63	Pd@COF-102	64	Pt/aUiO-C	65	Ni-doped ACNF	66
COF-301-$CoCl_2$	67	COF-301-$NiCl_2$	67	COF-301-$FeCl_2$	67	COF-350-$CoCl_2$	67
MgH_2 nanoparticles (4.5 nm)	68	MgH_2 nanoparticles (150 nm)	69	$NaBH_4$ nanosphere	70	$NaBH_4$ nanoparticles	71
$NaBH_4$-ODA	72	$NaBH_4$-DDA	72	$LiBH_4$-DDA	73	$LiBH_4$-$C_{18}NH_2$-5%	74
Nano-$LiBH_4$	75						

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