Review article

Transition metal-based novel catalysts for improving the sorption kinetics of MgH₂: current state-of-art

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Abstract

In the realm of solid-state medium for storing hydrogen, Mg-hydride (MgH_2) has emerged prominently due to its remarkable ability to store hydrogen, favourable reversibility, and cost-effectiveness, drawing recent attention. Still, due to its kinetic and thermodynamic nature, MgH_2 faces substantial challenges in its practical application. Two easy-to-use yet potent strategies for creating high-performance magnesium (Mg)-based hydrogen storage materials include doping catalysts and nanostructuring. This article evaluates several parameters that impact catalytic performance, such as oxygen vacancy, metal ion valance state, defect density, etc., making metal oxide-based catalysts an excellent option in this context. To provide a coherent description of the reaction mechanism, lower the activation energy barrier, increase the sorption rate, and other pertinent parameters controlling the kinetics of the reaction, a variety of binary along with ternary metal oxides have been considered. In this review summarizes the metal oxide and core-shell nanostructure Mg-based hydrogen storage materials: their hydrogen absorption and desorption processes. The evaluation ends with a plan for realistic future changes that might potentially improve the whole hydrogen sorption in magnesium hydroxide. So, it is proposed that before creating more catalysts, A broad knowledge of the reaction process for kinetic enhancement is necessary. An ideal catalyst for realizing practical utility will evolve from clear knowledge.

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Introduction

Until now,traditional energy resources like coal, natural gas, and petroleum have dominated as the primary means of energy production, constituting approximately 80% of the world's total energy consumption. This universality can be related to their extraction process as well as the comparatively simple logistics and technology needed to obtain energy from these fossil fuels. (Yan et al., 2024)(Prachi R. et al., 2016) fig.1Even though the natural supply of these resources is enormous, it is not endless, and over many centuries, human usage has greatly reduced a significant portion of it. Several experts from throughout the globe have possibly determined when these supplies will run out completely(Rathi et al., 2024).
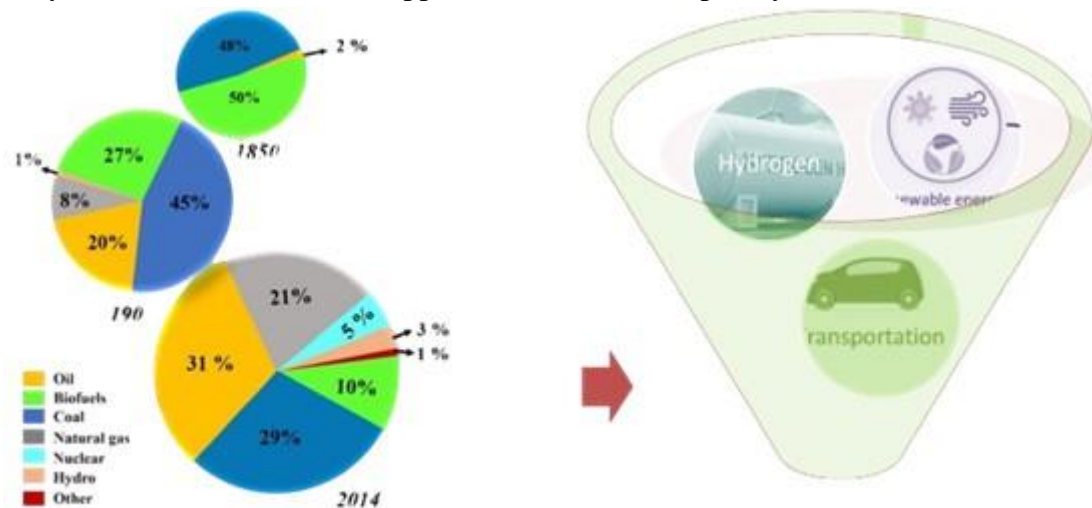

Fig-1 Shows how the global primary energy supply has changed over time and the futuristic approach to the hydrogen economy.

To be able to maximize the efficiency of renewable energy sources, especially for the transport industry, there exists an urgent require for effective energy storage systems. — referred to as secondary energy—that allow for on-demand release and mobility. Among the diverse array of secondary energy sources derived from various primary energy resources, hydrogen energy stands out as an encouraging alternative. The energy source is clean and suitable to the environment, offering the potential for near-zero emissions (Moradi & Groth, 2019). Recently, there has been a lot of research focused on renewable energy sources, which include hydrogen, solar, wind, as well as nuclear power. Hydrogen has emerged as a highly promising alternative in the current energy landscape, primarily due to its remarkable gravimetric energy density, which stands at 142 MJ kg $^{-1}$, surpassing that of other energy carriers (Momirlan & Veziroglu, 2005). These energy sources are well known. for their environmental friendliness and the potential for a nearly limitless supply. Hydrogen energy, in particular, has been a focal point of extensive research in recent years, driven by several compelling factors: (i) it stands as the most abundant element, comprising around 15 mol% of the Earth's surface and present in water, fossil fuels, and biomass; (ii) it possesses the lowest

molar mass at 2.016 g/mol, contributing to its lightweight nature; and (iii) it exhibits an impressive energy density of 141.2 MJ/kg.
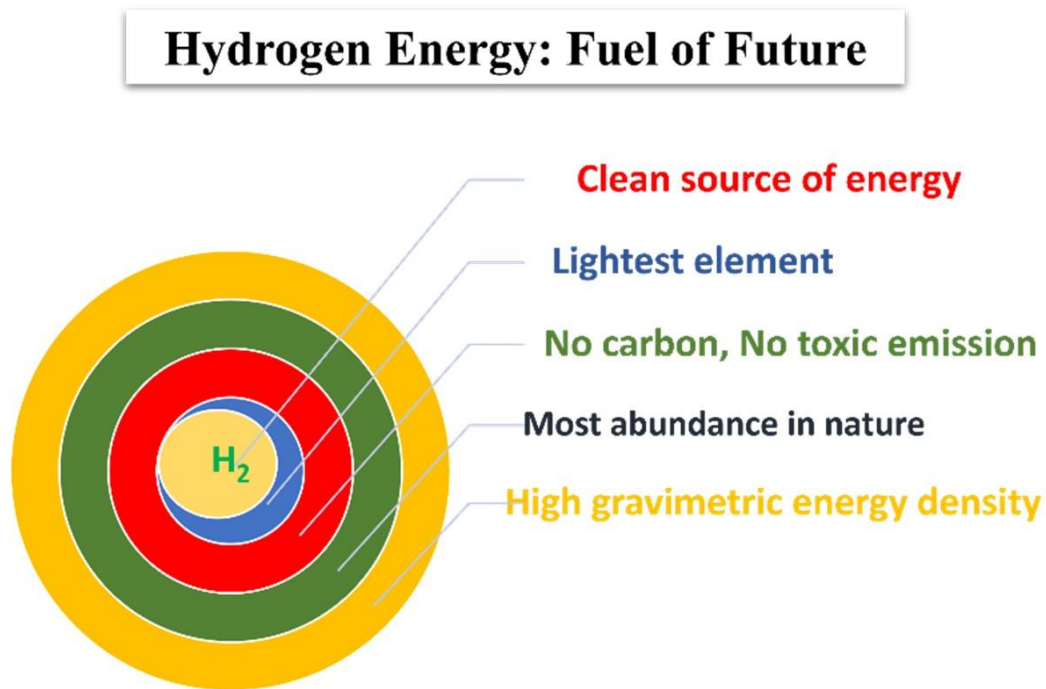
Hydrogen Energy: Fuel of Future

- **Clean source of energy**
- **Lightest element**
- **No carbon, No toxic emission**
- **Most abundance in nature**
- **High gravimetric energy density**

H_2

Fig-2 Represents the properties of hydrogen energy.

The storage of hydrogen can be accomplished through three main methods: (i) in compressed gaseous form, (ii) as a liquid at cryogenic temperatures, and (iii) within solid-state materials](J. Li et al., 2018). Gas storage facilities pose the risk of explosions because of the high-pressure conditions required for storing hydrogen. Cryogenic storage facilities entail complex technology and come with a high cost. In contrast, storing hydrogen in solid materials offers advantages such as easy controllability, moderate working pressure, and temperature (Graetz, 2012). Solid hydrogen storage materials have several advantages, including high storage capacity, enhanced safety features, and cost-effectiveness. Many kinds of materials for storing hydrogen have been created in recent decades; these materials include carbon nanotubes, metal hydrides, complex hydrides, metal-organic frameworks (MOFs), and more. Solid-state materials that store hydrogen can be generally divided into two types: (i) physical adsorption and (ii) chemical absorption. When it comes to materials with massive surface areas and porous structures, hydrogen molecules can undergo the process of adsorption on the surface and within pores through physisorption, facilitated by interactions between van der Waals. Hydrogen atoms can form chemical associations with metallic elements in cases of metal hydrides, which include elemental, complex, and intermetallic hydrides. Approximately 36 metallic elements can interact with hydrogen atoms, with magnesium (Mg) standing out as a particularly promising material for hydrogen storage applications. Its wide availability, low density, low toxicity, and remarkable gravimetric and

volumetric hydrogen storage capacities—which even surpass the standards established by the US Department of Energy (DOE)—are the reasons behind this(Chen et al., 2021).

Analysing the kinetics of hydrogen absorption in magnesium hydride (MgH$_2$) highlights how important a catalyst is to increase the sorption process's efficiency.

Magnesium-based hydride continues to receive a lot of attention because of its promising qualities as a material that can properly store hydrogen and heat energy. These characteristics include good reversibility, cost-effectiveness, and a high hydrogen storage capacity (7.6 wt%).
some disadvantages of magnesium hydride
(1) Slow kinetics
(2) desorption temperature high($>300^0$C) (Zhou et al., 2019)
Numerous groundbreaking research studies, along with outstanding review articles, have been published, aiming to enhance the performance of the MgH$_2$/Mg hydrogen storage system. For shipboard use, it is not feasible to achieve both the absorb and release of hydrogen in practical applications because achieving so requires degrees to be continuously at or above 300°C for several hours(Prachi R. et al., 2016).

Kinetics
The rate at which a material absorbs or desorbs hydrogen is dictated by the kinetics of sorption. This process is notably influenced by diverse material properties, including morphology, microstructural features, particle size, surface composition, particle dimensions, and the concentration of catalysts(Dornheim, 2011)(Graetz, 2012).The optimal functioning temperature of numerous hydrides often deviates from the value calculated through thermodynamics. The reason for this disparity is that the reaction's kinetics create an energy barrier(Graetz, 2012).
The kinetic barrier usually increases the operating degrees of the reaction. An intensive amount of research in this field is hence focused on bringing down the operating temperature to obtain enhanced kinetics in hydridematerials. Theoretical investigations have validated that lowering the size of the particles of Mg/MgH$_2$ leads to a minimization in the enthalpy value of MgH$_2$. Consequently, the thermodynamic characteristics of MgH$_2$ are significantly impacted by the notable decrease in the dehydrogenation temperature(Du et al., 2005).(fig 3).
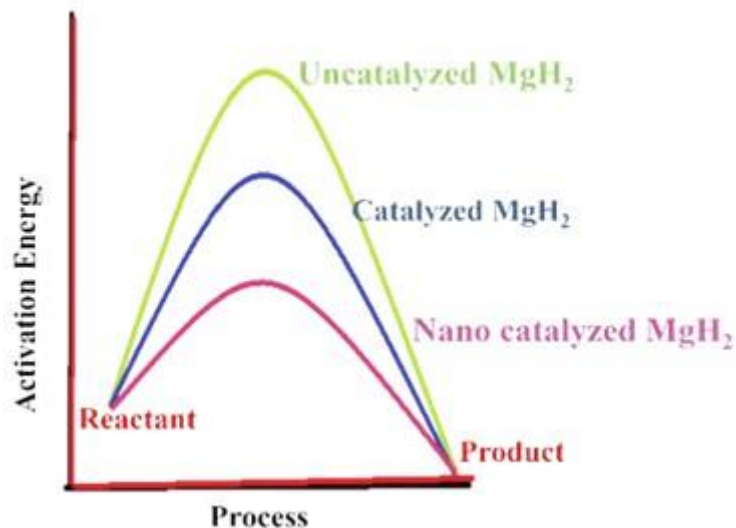
Fig-3 shows a bar graph comparison of the activation energy of the MgH_2 system when it is uncatalyzed, catalyzed, and noncatalyzed.

**Use of catalyst to enhance magnesium hydride kinetics.**

Catalysts play a pivotal role in augmenting the hydrogen absorption rate by weakening the Mg–H bond, consequently reducing the bonding energy within the catalyzed magnesium hydride system (Xie et al., 2013). The most efficient and straightforward way to improve the kinetic performance of the hydrogen absorb and desorb reaction in MgH_2 is by utilizing catalysts, which increase the reaction's active regions and accelerate it(Hou et al., 2021). The thermodynamic and kinetic performance of Mg/MgH_2 in the dehydriding/hydriding processes has been tweaked by a wide range of methods, such the introduction of catalysts, adding with metals to make alloys, and nano crystallization.The use of nanostructured Mg-based materials can reduce the diffusion pathway, facilitating the transport of H atoms and leading to a significant enhancement in the rate of hydrogen absorption and desorption for Mg-based hydrogen storage materials. As an illustration, Xia et al. fabricated nanoparticles of MgH_2 supported on graphene and coated with uniformly distributed nanosized Ni catalysts (Ma et al., 2018).

Mechanism for catalyst enhanced MgH_2 system

While the quest for new, improved catalysts is ongoing, there remains a lack of comprehensive comprehension regarding catalytic mechanisms. The notion of a hydrogen spillover phenomenon has been advocated in catalysts reliant on metals, wherein metal particles initially capture H_2 before disseminating it throughout the entire structure(Y. Li & Yang, 2006).

Metal particles (such as Ti, Pd, and Ni,Cu) tend to first capture and spillover hydrogen to the magnesium surface during the catalytic phase, which lowers the potential barrier to H_2 dissociation. The existence of many valance states in TM facilitates the breakdown of hydrogen molecules and the subsequent transport of hydrogen atoms to the nearest magnesium atoms. The spillover process is thought to consist of three steps.In the initial

stage, H_2 molecules disperse across the entire surface of the composite material through diffusion.

$$Mg + H_2 \leftrightharpoons MgH_2$$
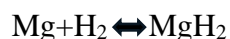
- Following diffusion, chemisorption occurs, wherein H_2 molecules bond with the metal nanoparticle in their elemental form.
- Subsequently, hydrogen atoms undergo dissociation from the metal particles and spread throughout the entire Mg matrix(Zhang et al., 2016).

Transition Metal

Because they have d-orbital electrons, which can serve as electron transfer media and allow hydrogen to dissociate and combine on the surface, transition metals are typically employed as catalysts(Cui et al., 2014), (Zhang et al., 2021). By using mechanical milling to create nanocomposite powders of MgH_2–TM (TM = 3d transition elements Ti, V, Mn, Fe, and Ni), phase transitions during the absorption and desorption processes were investigated. Catalysts in the form of TiH_2, $VH_{0.81}$, Mg_2FeH_6, and Mg_2NiH_4 phases were identified within the Mg–Ti, Mg–V, Mg–Fe, and Mg–Ni composites, respectively. In the case of Mg–Mn, manganese persisted in its metallic state (Liang et al., 1999).conducted research on composites comprising $MgH_2 + 5wt\%T_m$ (where Tm = Ti, V, Mn, Fe, Ni) to explore hydrogen desorption behaviorswithin the mixture. Their results showed that all doped composites exhibited superior absorption kinetics compared to undoped MgH_2. Furthermore, the catalytic impact varied among the five metals (Ti, V, Mn, Fe, Ni). Composites containing Ti displayed the most favorable absorption kinetics, while $MgH_2 + 5wt\%V$ showed the swiftest desorption kinetics at lower temperatures among the metal-doped composites. To delve deeper into the catalytic influence of vanadium, they ball-milled a mixture of magnesium hydride and 15 wt % vanadium. Vanadium hydride functioning as a hydrogen pump was identified as the cause of the observed sped up kinetics, together with elements like increased specific area, reduced particle size, and the introduction of defects(Liang et al., 2000).

(Lu et al., 2017) successfully synthesized core-shell structured Mg@TM (TM = Co, V) composites using a combination of the arc plasma method and electroless plating. Their results revealed that the hydrogen absorption/desorption enthalpies for Mg@Co@V (70.02/74.83 kJ/mol H_2) were lower compared to those for Mg@Co (73.25/81.47) and Mg@V (73.91/79.77) samples. Additionally, the activation energy (Ea) values were 73.22 kJ/mol H_2 for Mg@Co, 86.30 kJ/mol H_2 for Mg@V, and 67.66 kJ/mol H_2 for Mg@Co@V, which were all less than the value of pure ultrafine magnesium powder. (118.20 kJ/mol H_2). The improved performance can be attributed to the catalytic activities of V and Co, as well as the core-shell microstructures.

(Cui et al., 2014) applied a method involving high-energy pre-milling of Mg powder with corresponding chlorides ($TiCl_3$, $NbCl_5$, VCl_3, $CoCl_2$, $MoCl_3$, and $NiCl_2$), followed by electroless plating, to coat Mg with TM (TM = Ti, Nb,Cu,Fe, V, Co, Mo, or Ni) and its compounds, forming a composite material with Mg as the core and the respective TM as the shell. The Mg–Ti composite exhibited superior hydrogen storage performance compared to others. According to their research, metals with less electronegativity showed more catalytic activity when it came to magnesium nanoparticles. Additionally, noble metals displayed significant catalytic activity for Mg-based hydrogen storage materials.(Lu et al., 2019)

synthesized core–shell nanostructured Mg@Pt material via a plasma–solid reaction method. In situ TEM observations and density of the functional theory calculations revealed that metastable H stabilized the Mg_3Pt particles formed on the interface, acting as a "hydrogen pump" to accelerate the hydrogen absorb and desorb rate of Mg/MgH_2.

Catalytic properties of different metal oxides
For certain purposes, Metal oxides make good possibilities for catalysis and help in catalyzing reactions under particular conditions.
1. Strong attraction to hydrogen.
2. Facilitate hydrogen dissociation and recombination.
3. Assist in overcoming the MgO layer's surface passivation.
4. Bonding sites.
5. Surface field presence due to the lattice's coulombic nature.
6. Encourages surface spanning with functional group.
7. Oxygen accessibility: oxygen hopping, and vacancies are possible.

Hydrogen often creates a strong O–H bond with an almost oxygen ion in metal oxides, and as a result, shows incredible stability. Hydrogen and metal oxide usually interact at lower temperatures or even at ambient temperatures.

Table:1 The desorption and absorption kinetics for pristine MgH_2catalyzed with different binary metal oxides & ternary metal oxides.

S.No	Metal Oxide	Process	Desorption findings	Absorption findings	Activation energy (KJ/mol)	Ref.
[1]	TiO_2 5 wt %	Arc plasma method	Desorption started from 405 °C	6.2 wt % H_2 at 250 °C in 600 s.	77.2	(Yadav et al., 2021)
[2]	VO_2 10 wt%	Milled for 10 h	Desorption maxima at 642 K		139	(Dan et al., 2019)
[3]	MnO_3 2 mol %	Ball milled for 10 hrs with 400 rpm	5 wt % H_2 at 300 °C in 900s	% 4.2 wt % H_2 at 282 °C in 900s	114.7	(Song et al., 2021)
[4]	Fe_3O_4 10 wt %	Ball milled under 6 bar Ar pressure	Desorption temperature at 384.31 °C	-	231.90	(B.-H. Chen et al., 2016; Kimura et al., 2013)

[5]	Nb_2O_5 1 mol%	Ball milled for 20 h with 400 rpm	4.5 mass% H_2 in 15 s at RT under 1 MPa pressure	6wt % H_2 at 160 ∘C	71	(Kimura et al., 2013)
[6]	Y_2O_3/NiO 10 wt%.	ball milled for 5 h with 500 rpm	6.6 wt% H2 275 ∘C in 60 min	4.2 wt% H_2 at 150 ∘C in 50 min.	86	(L. Zhang et al., 2021)
[7]	$TiNb_2O_7$ (7 wt %)	Solvothermal Nanospheres	5.5 wt% H_2 at 250 ∘C in 10 min	4.5 wt% H_2 at 150 ∘C in 3 min	96 ±4/139 ±7	(Xian et al., 2022)
[8]	$NiMoO_4$ 10 wt%	Hydrothermal Nanorods	6 wt% H_2 at 300 ∘C in 10 min	5.5 wt% at 150 ∘C under	85.88 ±0.36/ 145.08 ±3.01	(Juahir et al., 2015)
[9]	$NiTiO_3$ (6 wt %)	Sol-gel method Nanorods	~0.64 wt%/min at 300 ∘C	-	74 ±4	(J. Zhang et al., 2015)
[10]	$MgNiO_2$ 10 wt%	hydrothermal Nanoflakes	5.1 wt% H_2 at 340 ∘C in 10min	6.1 wt% at 200 ∘C in 10 min	52/108	(T. Zhang et al., 2014a, 2014b)
[11]	$BiVO_4$ 16.7 wt%	Solvothermal nanoparticles	1.1 wt% H_2 at 573 K in 1200 s	1.99 wt% of H_2 at 423 K under 3 MPa	84.33/122.29	(Yang et al., 2023; T. Zhang et al., 2014b)
[12]	$BaFe_{12}O_{19}$ 10 wt%	solid-state reaction Nano-powder	3.5 wt% H_2 at 320 ∘C in 15 min	4.3 wt% H_2 at 150 ∘C in 17 min	115/144	(Mustafa et al., 2016)
[13]	$MnMoO_4$ 10 wt%	Hydrothermal method Nanorods	6 wt% H_2 within 10 min at 300 ∘C.	4.34 wt% H_2 at 150 ∘C and 3 MPa H_2 pressure in 15 min	109.9/154.9	(X. Zhang et al., 2018)

Core-shell nano magnesium-based hydrogen storage materials.

Many scientists have created core-shell nanostructured magnesium@ transition metals, where the transition metal (TM) serves as the shell layer, and they have methodically investigated the process by which these metals store hydrogen.

Table:2 The storage of hydrogen in typical core-shell nanostructured magnesium-based materials.

S.No	Material	Process	Desorption findings	Absorption findings	Activation energy (KJ/mol)	Ref.
[1]	Mg–Nb	Electrolessplating	2.5wt%/250°C/1kPa/10min	4.2wt%/225°C/2MPa/5min	48.2	(Cui et al., 2013)
[2]	Mg–Ni	Electrolessplating	0.7wt%/250°C/1kPa/10min	5.8wt%/225°C/2MPa/5min	51.2	(Cui et al., 2013)
[3]	Mg–Ti	Electrolessplating	-	2.2wt%/250°C/2.8MPa/10min	72.2	(Lu et al., 2017)
[4]	Mg–Ni	Electrolessplating	-	4.7wt%/250°C/2.8MPa/10min	88.9	(Zou et al., 2012)
[5]	Mg–Ni–Ti	Electrolessplating	-	2.5wt%/250°C/2.8MPa/10min	63.7	(Lu et al., 2017)
[6]	Mg–Gd_2O_3	Arcplasma&passivation	-	2.4wt%/300°C/4MPa/5min	59.3	(Zou et al., 2013)
[7]	Mg–LaF_3	Arcplasma	-	6.2wt%/200°C/3MPa/120min	73.0/185.8	(Liu et al., 2019; Mao et al., 2017)
[8]	Mg–Ni–Ti_3C_2	Ballmilling	5.2wt%/250°C/2kPa/15min	5.4wt%/125°C/3MPa/25s	56/73	(M. Chen et al., 2019; Liu et al., 2019)
[9]	Mg–V–C	Reactivegasevaporation	5.2wt%/300°C/0.1kPa/60min	5.5wt%/200°C/4MPa/45min 78	41/67	(M. Chen et al., 2019)
[10]	Mg–Ni-	Nanoconfinement	1.5wt%/325°C/2kPa/150s	1.2wt%/150°C/3MPa/60min	41.5/144.7	(Jia et al., 2013)

|					
MOF					

Core-shell nanostructured magnesium-based hydrogen storage materials offer exciting potential for various applications

Long-term cycle performances and good hydrogen uptake and release kinetics are demonstrated by core-shell nanostructured magnesium-based hydrogen storage materials.Due to their unique structure, composites have several exceptional qualities, like the ability to resist air oxidation and a quick rate of hydrolysis. Considering the, we propose a promising future use of core-shell nanostructured magnesium-based hydrogen storage materials (Fig. 4)(Li et al., 2023).Furthermore, the unique reversibility of core-shell nanostructured magnesium-based materials is protected by their shell topologies, which qualifies them for industrial application. Furthermore, magnesium-based core-shell nanostructured materials show exceptional hydrolysis capabilities. A magnesium hydroxide coating will develop on the surface of pristine magnesium particles during the hydrolysis process, which will impede the hydrolysis reaction's advancement.(Berezovets et al., 2021)
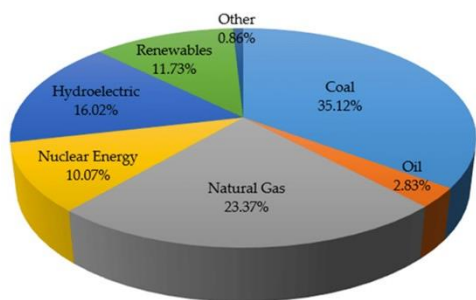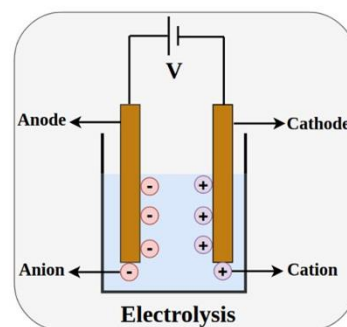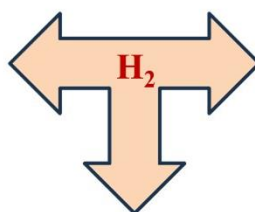
Fig-4 Avision of the future application of core-shell structured Mg-based hydrogen storage materials.

Summary and outlook

The production of MgH$_2$ family composites, which have a high energy density, low cost, good reversibility, and a high hydrogen storage capacity, has emerged as one of the primary study areas in the "Hydrogen Economy" subject. In response to the problem of Mg/MgH$_2$'s inadequate kinetic performance and cycling performance, researchers have examined a broad spectrum of metal-based catalysts, such as those based on manganese, nickel, iron, titanium, vanadium, and titanium alloys, all of which have improved Mg/MgH$_2$'s kinetic performance and cycling performance to varying degrees.

In addition to the type of catalyst, the amount of catalyst has been found to have a significant effect on its hydrogen uptake rate in these materials. The kinetic characteristics of several of the intriguing candidates, such as Nb$_2$O$_5$, TiO$_2$, Cr$_2$O$_3$, and Fe$_2$O$_3$, are covered in detail in the section on binary metal oxide catalysts. Additionally, several teams have investigated combining two metal oxide-based catalysts, and their findings indicate a reduction in the activation energy barrier that is larger than that of the metal oxides employed alone. In literary works, this phenomenon has been called the "Synergistic" effect. Ternary metal oxides are made up of two or more metals and have also been extensively researched as catalysts. This review explains TM-TM, Alkali Metal-TM, and Alkali Rare Earth-TM, which outperform their binary counterparts in catalysis frequently time.

To enhance the qualities of hydrogen storage of advanced core-shell nanostructured Mg/MgH$_2$ nanoparticles and balance costs and benefits, it is particularly crucial to determine the best technical paths and processing parameters. These nanoparticles should be smaller and have a better catalytic shell. To meet the criteria for industrial applications, it is known that much better thermodynamic, kinetic, and cycle performances can be produced by effectively integrating the size effect of the magnesium core with the catalytic impact of the shell.

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