Role of Microstructure and Spectral Features in the Catalytic Effect of Ce1-x(Nd0.5Eu0.5)xO2-d Solid Solutions Postprint

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Abstract

Nanosized Ce1-x(Nd0.5Eu0.5)xO2-d solid solutions (x = 0.00∼0.20) were synthesized by means of hydrothermal method. Then the solid solutions were ball milled with Mg2Ni and Ni powders for 20 h to get the Mg2Ni–Ni–5 mol% Ce1-x(Nd0.5Eu0.5)xO2-d composites. The structures and spectrum characteristics of the Ce1-x(Nd0.5Eu0.5)xO2-d solid solutions catalysts were analyzed systemically. XRD results showed that the doped samples exhibited single phase of CeO2 fluorite structure. The cell parameters and cell volumes were increased with increasing the doped content. Raman spectrum revealed that the peak position of F2g mode shift to higher wavenumbers and the peak corresponding to oxygen vacancies were observed distinctly for the doped samples. UV-Vis technique indicated that the absorption peaks of Eu3+ and Nd3+ ions appeared; the bandgap energy was decreased linearly. The electrochemical and kinetic properties of the Mg2Ni–Ni–5 mol% Ce1-x(Nd0.5Eu0.5)xO2-d composites were measured. The maximum discharge capacity was increased from 722.3 mAh/g for x = 0.00 to 819.7 mAh/g for x = 0.16, and the cycle stability S20 increased from 25.0% (x = 0.00) to 42.2% (x = 0.20). The kinetic measurement proved that the catalytic activity of composite surfaces and the hydrogen diffusion rate were improved for the composites with doped catalysts, especially for the composites with x = 0.16 and x = 0.20. The catalysis mechanism was analyzed from the point of microstructure and spectrum features of the Ce1-x(Nd0.5Eu0.5)xO2-d solid solutions.

Full Text

Role of Microstructure and Spectrum Features on the Catalysis Effect of Ce1-x(Nd0.5Eu0.5)xO2- Solid Solutions

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ABSTRACT

Nanoscale Ce1-x(Nd0.5Eu0.5)xO2- solid solutions (x = 0.00–0.20) were synthesized via a hydrothermal method and subsequently ball-milled with Mg2Ni and Ni powders for 20 h to prepare Mg2Ni–Ni–5 mol% Ce1-x(Nd0.5Eu0.5)xO2- composites. The crystalline structures and spectral characteristics of the Ce1-x(Nd0.5Eu0.5)xO2- catalysts were systematically analyzed. XRD results confirmed that all doped samples exhibited a single-phase CeO2 fluorite structure, with both unit cell parameters and volumes increasing as dopant content rose. Raman spectroscopy revealed a shift in the F2g mode peak toward higher wavenumbers and clearly resolved peaks corresponding to oxygen vacancies in the doped samples. UV-Vis analysis showed characteristic absorption peaks for Eu3+ and Nd3+ ions and a linear decrease in bandgap energy. Electrochemical and kinetic measurements demonstrated that the Mg2Ni–Ni–5 mol% Ce1-x(Nd0.5Eu0.5)xO2- composites exhibited enhanced performance, with maximum discharge capacity increasing from 722.3 mAh/g (x = 0.00) to 819.7 mAh/g (x = 0.16) and cycle stability S20 improving from 25.0% (x = 0.00) to 42.2% (x = 0.20). Kinetic analysis confirmed improved catalytic activity at composite surfaces and enhanced hydrogen diffusion rates, particularly for composites with x = 0.16 and x = 0.20. The catalysis mechanism is discussed in terms of the microstructure and spectral features of the Ce1-x(Nd0.5Eu0.5)xO2- solid solutions.

Keywords: hydrothermal method; Ce1-x(Nd0.5Eu0.5)xO2- solid solutions; Mg2Ni; ball milling; catalysis mechanism

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1 INTRODUCTION

Research on hydrogen storage properties of Mg-based alloys has attracted considerable attention due to their high theoretical capacity, earth abundance, and low cost. However, practical applications as negative electrode materials in Ni/MH batteries remain hindered by poor cycle stability and slow sorption/desorption kinetics. Numerous efforts have been devoted to overcoming these limitations, with improvements typically achieved through nanocrystallization and/or addition of various catalysts or additives [1, 2]. Ball milling represents one of the most effective and straightforward methods for producing nanoscale materials with abundant fresh surface areas and numerous defects both on the surface and within the bulk of alloy powders [3]. Various catalysts have been incorporated into Mg-based systems, demonstrating outstanding catalytic properties. Among these, metal oxides constitute a particularly important and effective class of catalysts that has been extensively investigated. Compared with metallic catalysts, metal oxides can disperse more uniformly on Mg-based alloy surfaces due to their brittleness, while the local electronic structure of the catalysts also plays a crucial role [4, 5]. Previous reports indicate that oxides are reduced to lower valence states and their local structures become disordered after ball milling with MgH2 [6], and that interactions between metal oxide catalysts and Mg-based hydride surfaces can enhance desorption kinetics [7].

Over the past decades, the catalytic properties of CeO2 and CeO2-based materials have been thoroughly investigated owing to their unique structures and distinctive electronic characteristics, leading to widespread applications in three-way catalysts (TWC) [8, 9], water-gas shift catalysts (WGS) [10], and various oxidation catalysts [11, 12]. The catalytic effects primarily depend on the activity of the Ce4+/Ce3+ redox couple, which can more readily change valence (1.3-1.8 V) under different conditions compared to other metal oxides. Another key feature is the formation of oxygen vacancies in the bulk or on the surface of CeO2, which significantly influences catalytic activity. Various cations with different ionic radii and valences have been doped into the CeO2 lattice to form CeO2-based solid solutions, inducing additional oxygen vacancies and structural distortion. These modifications create active phases at catalyst interfaces and generally lead to improved catalytic performance [13-15]. Extensive research has shown that doping with di- or trivalent ions is a primary strategy for significantly enhancing catalytic activity, as these ions partially replace Ce4+ and generate substantial oxygen vacancies in the lattice [16-18].

CeO2 has been reported to react with H2 [11], and CeO2-based catalysts have attracted increasing attention for hydrogen storage applications, though opinions on the catalytic mechanism vary. Several studies have examined the effects of CeO2 on hydrogen storage properties of Mg-based alloys, demonstrating its beneficial impact on MgH2 sorption behavior [19]. Notably, while pure CeO2 appears ineffective for hydrogen desorption kinetics, Pt-doped CeO2 shows positive effects [20]. Jelena et al. [21] investigated the influence of nanoscale CeO2 on hydrogen desorption from MgH2, attributing the catalytic effect to the non-stoichiometric structure and oxygen vacancies in CeO2, where small polarons act as promoters for catalytic activity. From a microscopic perspective, hydrogen atoms tend to penetrate along the (110) facet of CeO2 [22], and electronic exchange reactions occur between Mg-based hydrides and catalysts, weakening Mg–H bond energies and consequently improving hydrogen desorption kinetics. Our group has previously studied the catalytic effects of doped and undoped CeO2 on Mg-based alloys, finding that doped CeO2 solid solutions consistently perform better. Their catalytic performance is closely linked to dopant species and content, as well as spectral and structural characteristics during the catalysis process [23]. However, the specific roles of factors such as crystal structure, spectral characteristics, and electronic structure during catalytic reactions remain unclear.

Nd3+-doped CeO2 has been reported to exhibit the highest hole conductivity [24], and the resulting solid solutions show enhanced catalytic activity for methane total oxidation [25]. Additionally, Ce1−xEuxO2−x/2 mixed oxides demonstrate superior catalytic performance for CO oxidation, attributed to increased oxygen vacancy concentrations [26]. Therefore, this work synthesizes Nd3+ and Eu3+ co-doped nanoscale CeO2-based solid solution catalysts, systematically investigates their crystalline structures and spectral features, evaluates their catalytic effects on the electrochemical performance of ball-milled Mg2Ni, and analyzes the catalysis mechanism from the perspectives of microstructure and spectral characteristics.

2 EXPERIMENTAL

2.1 Sample Synthesis

Ce(NO3)3 · 6H2O (AR), Nd(NO3)3 · 6H2O (AR), Eu(NO3)3 · 6H2O (AR), and NaOH (AR) were used as starting reagents to synthesize Nd3+ and Eu3+ co-doped Ce1-x(Nd0.5Eu0.5)xO2- solid solutions via a hydrothermal method. The synthesis procedure was as follows: lanthanide nitrate solutions were prepared at 0.3 mol/L concentration and mixed in specific proportions with dopant content x varying from 0.00 to 0.20. Subsequently, 6 mol/L NaOH solution was added as a mineralizer to adjust pH to approximately 12. The resulting suspensions were sealed in Teflon-lined autoclaves and heated at 200 °C for 24 h. The products were thoroughly washed with distilled water and dried at 80 °C for 6 h. The as-prepared Ce1-x(Nd0.5Eu0.5)xO2- solid solutions were then mixed with Mg2Ni powders (200 mesh) and Ni powders (200 mesh) at a weight ratio of 0.05:1:1 and ball-milled for 20 h. The ball milling process was conducted in stainless steel containers under Ar atmosphere with a ball-to-material weight ratio of 40:1 and a jar rotation speed of 350 rpm.

2.2 Characterization

The phase composition of the solid solutions was determined by X-ray diffraction (Rigaku DAMX2500) using CuK radiation. Average particle size D was calculated from the CeO2 (111) diffraction peak using the Scherrer formula, and lattice parameters were refined by full-matrix least-squares methods. Diffuse reflectance UV-Vis spectroscopy was recorded on a Hitachi U-3900 spectrophotometer. Raman spectra were measured on a JY-HR800 spectrometer with a He-Ne laser (excitation wavelength 418 nm, output power 20 mW) in the 200-

1000 cm-1 range. Electrochemical and kinetic property measurements of Mg2Ni-based compounds followed procedures described in our previous report [23], with Mg2Ni alloy weight considered as the active material.

3 RESULTS AND DISCUSSION

3.1 XRD Characterization

Fig. 1 [Figure 1: see original paper] shows XRD patterns of pure and Nd3+/Eu3+ co-doped CeO2 samples. All samples with dopant content x from 0.00 to 0.20 exhibited typical fluorite cubic structure (space group fm3m) without any detectable secondary phases corresponding to dopant compounds. Although the solid solutions maintained single-phase structure, doping induced subtle lattice transformations. The inset in Fig. 1 displays enlarged (111) peaks, which gradually shift to lower angles compared with undoped CeO2, indicating lattice expansion following Vegard’ s law. Notably, the (111) peak for x = 0.20 slightly shifts back to higher angle, attributed to crystallite size effects (Fig. 2 Figure 2: see original paper). Lattice parameters serve as sensitive indicators of lattice structural changes and chemical composition, and are commonly used to estimate solid solubility [27]. Both Eu3+ (1.066 Å) and Nd3+ (1.109 Å) ionic radii exceed that of Ce4+ (0.97 Å) in 8-coordination; therefore, substitution of Ce4+ by dopant ions should increase cell parameters and volumes.

Indeed, Fig. 2(a) shows a systematic increase in cell parameters with dopant content, with similar trends observed for cell volumes in Fig. 2(b), confirming dopant incorporation into the CeO2 lattice and formation of homogeneous Ce1-x(Nd0.5Eu0.5)xO2- solid solutions. Fig. 2(c) presents crystallite sizes calculated from the Scherrer formula, showing strong dependence on dopant content. Size decreased sharply from 23 nm for pure CeO2 to 12 nm at x = 0.04, then increased continuously with further dopant addition, followed by a slight decrease at x = 0.20. Multiple factors influence lattice variation, primarily dopant valence states and crystallite size. Generally, lattice contraction occurs with increasing crystallite size due to microstrain effects in nanomaterials [28]. However, combining results from Fig. 2(a) and 2(c) reveals that despite crystallite size growth, cell parameters increase linearly, indicating dopant content is the primary factor affecting cell parameters.

3.2 Raman Spectra

Raman spectroscopy provides a nondestructive, sensitive, and rapid technique for investigating phonon and electronic structures, where changes in lattice spacing or chemical environment induce band frequency shifts. CeO2 adopts a cubic fluorite structure belonging to the space group. Doping Nd3+ and Eu3+ into the CeO2 lattice causes structural distortion detectable by Raman spectroscopy.

Fig. 3 [Figure 3: see original paper] displays Raman spectra of typical Ce1-x(Nd0.5Eu0.5)xO2- solid solutions. All samples show a sharp, intense band near 453 cm-1 corresponding to the Raman-active F2g mode, characteristic of fluorite structures and representing oxygen breathing vibrations around Ce4+ ions [29]. The shift of the F2g mode to higher wavenumbers in doped samples arises from crystallite size effects and lattice distortion [30]. Additionally, a broad, weak peak near 570 cm-1 appears, characteristic of oxygen vacancies in the Ce1-x(Nd0.5Eu0.5)xO2- lattice, with intensity increasing with dopant content.

3.3 UV-Vis Spectrum Analysis

UV-Vis absorption spectra of Ce1-x(Nd0.5Eu0.5)xO2- (x = 0.00-0.20) solid solutions are shown in Fig. 4 Figure 4: see original paper. Pure CeO2 shows no visible region absorption, while doped samples exhibit additional absorption peaks whose intensities become more pronounced with increasing Nd3+ and Eu3+ concentrations. Weak bands at 520 and 534 nm correspond to 4f-4f transitions from the 7F0,1 level to excited states of Eu3+ ions: specifically, the 520 nm band arises from 7F0 → 5D1 transition, while 7F1 → 5D1 occurs at 535 nm [30]. More intense bands centered near 590, 685, and 745 nm correspond to Nd3+ transitions from the 4I9/2 ground state to higher levels 4G5/2 + 4G7/2, 4F9/2, and 4F7/2 + 4S3/2, respectively [31]. Fig. 4(b) presents bandgap energies calculated using the Tauc relation for direct allowed transitions (Eq. (1)):

$$\alpha h\nu = A(h\nu – E_g)^{1/2} \qquad (1)$$

where α is the absorption coefficient and A is a constant. Bandgap energies decrease nearly linearly from 3.23 eV (x = 0.00) to 2.81 eV (x = 0.20), attributed to replacement of Ce4+ by lower-valence Eu3+ and Nd3+ ions, resulting in oxygen vacancy formation and additional energy levels. Doping-induced lattice distortion also affects bandgap structure. These results corroborate Raman analysis, confirming successful Eu3+ and Nd3+ incorporation into the CeO2 lattice and consequent effects on lattice structure and electronic transition properties.

3.4 Microstructure of Mg2Ni-Ni-5% Ce1-x(Nd0.5Eu0.5)xO2- Composites

Fig. 5 [Figure 5: see original paper] shows XRD patterns of Mg2Ni-Ni-5% Ce1-x(Nd0.5Eu0.5)xO2- composites after 20 h ball milling. Mg2Ni alloys exhibit amorphous/nanocrystalline phases, while Ni powders retain crystalline structure (PDF#70-0989). Ce1-x(Nd0.5Eu0.5)xO2- phases are not observed, likely due to the small catalyst quantity. SEM images in Fig. 6 [Figure 6: see original paper] reveal uniform particle sizes of approximately 5 µm. XRD and SEM results show no significant morphological differences among composites with various catalysts, suggesting that variations in electrochemical and kinetic performance arise from catalytic effects of Ce1-x(Nd0.5Eu0.5)xO2- with different dopant contents.

3.5 Electrochemical Properties of Mg2Ni-Ni-5% Ce1-x(Nd0.5Eu0.5)xO2- Composites

Fig. 7 Figure 7: see original paper presents first-cycle discharge curves of ball-milled Mg2Ni-Ni-5% Ce1-x(Nd0.5Eu0.5)xO2- composites. The discharge potential plateau corresponds to hydrogen oxidation from Mg2NiH4. Comparison of catalysts with different dopant contents shows broader discharge potential plateaus for doped samples versus pure CeO2. Specifically, discharge capacity increases from 722.3 mAh/g (x = 0.00) to 819.7 mAh/g (x = 0.16), then slightly decreases to 780.1 mAh/g (x = 0.20), demonstrating that doped Ce1-x(Nd0.5Eu0.5)xO2- enhances discharge capacity relative to pure CeO2. Notably, electrodes with Ce1-x(Nd0.5Eu0.5)xO2- (x = 0.00, 0.12, 0.16) show similar mid-potentials, while composites (x = 0.08, 0.20) shift to higher potentials with steeper discharge slopes, attributed to varying amorphization tendencies [33].

Cycle stability is a critical feature affecting battery service life, along with activation characteristics and maximum discharge capacity. Fig. 7(b) depicts cyclic stability curves, with the inset showing maximum discharge capacity and capacity retention rate S20. All composites activate during the first cycle. Composites with doped Ce1-x(Nd0.5Eu0.5)xO2- exhibit higher maximum discharge capacities than those with pure CeO2, with S20 values increasing from 25.0% (x = 0.00) to 42.2% (x = 0.20). For Mg2Ni-based composites, capacity degradation primarily results from active alloy corrosion in alkaline electrolyte; the improved cycle stability suggests doped solid solutions likely enhance corrosion resistance of Mg2Ni alloys.

3.6 Electrochemical Kinetic Properties

Fig. 8 Figure 8: see original paper shows EIS Nyquist plots of Mg2Ni-Ni-5% Ce1-x(Nd0.5Eu0.5)xO2- composite electrodes at 50% depth of discharge (DOD). Each curve comprises two semicircles and linear Warburg impedance. The larger mid-frequency semicircle corresponds to charge transfer at the electrode surface, representing the rate-determining step at the alloy-electrolyte interface. Charge transfer rates depend on crystallographic and electronic structure [35], with surface composition affecting valence electron distribution and substantially influencing hydrogen dissociation reactions [36]. Composites with doped Ce1-x(Nd0.5Eu0.5)xO2- (x > 0.00) show visibly reduced large semicircle radii, indicating enhanced charge transfer rates. The catalytic activity order is: x = 0.20 > 0.16 > 0.12 > 0.08 > 0.00, consistent with dopant content.

To evaluate hydrogen diffusivity, Fig. 8 Figure 8: see original paper presents semilogarithmic anodic current log(i) versus time (t) curves at 100% DOD. From the log(i) vs. t slope, hydrogen diffusion coefficient D was calculated assuming an average composite radius of 10 μm [37]. The inset in Fig. 8(b) shows D initially increases then slightly decreases with dopant content, demonstrating that catalyst composition significantly influences hydrogen diffusion.

3.7 Catalysis Mechanism Explanation

As discussed, the electrochemical and kinetic properties of Mg2Ni–Ni–5% Ce1-x(Nd0.5Eu0.5)xO2- composites improve markedly, indicating that Eu3+ and Nd3+ co-doped catalysts positively promote hydrogen storage properties. The catalysis mechanism can be analyzed from microstructural and spectral perspectives. XRD, Raman, and UV-Vis analyses reveal that increasing dopant content enlarges cell parameters, distorts lattice structure, increases oxygen vacancy concentration, and decreases bandgap energies—all contributing to improved Mg2Ni alloy hydrogen storage properties.

Regarding cell parameters, Chafi et al. [22] proposed that H readily adsorbs along CeO2 (110) surfaces without energy barrier. Increased cell parameters provide larger interstitial space for H penetration, allowing more H atoms to enter the lattice. This enables H atoms to preferentially occupy CeO2-based catalyst sites rather than passivating Mg(OH)2 or MgO layers, which are primary causes of slow sorption/desorption kinetics in Mg-based alloys. Upon H absorption, the Mg–H bond in formed Mg2NiH4 remains influenced by catalysts through close interaction between electronic orbitals of catalysts and Mg2NiH4. Electronic exchange reactions weaken the Mg–H bond, accelerating Mg2NiH4 dissociation. Narrowed catalyst bandgap energies enhance electronic exchange interactions, facilitating Mg–H bond decomposition [21]. Concerning oxygen vacancies, catalytic activity depends strongly on their concentration. Oxygen vacancies and small polarons in CeO2’ s defective structure improve hydrogen desorption kinetics. Borgschulte et al. [38] demonstrated that MgH2 desorption properties correlate with oxygen vacancy formation, while Oelerich et al. [4] showed oxides with different valences exhibit superior catalytic effects. In this work, doping two ions of different valence and size into the CeO2 lattice increases oxygen vacancy concentration and creates diverse electronic states for metal atoms. Meanwhile, Ce1-x(Nd0.5Eu0.5)xO2- solid solutions maintain single-phase fluorite structure, enabling rapid oxygen diffusion within the same crystallographic plane—an important benchmark for catalytic activity.

Notably, although lattice distortion degree, bandgap energy, and oxygen vacancy content change nearly linearly, some hydrogen storage properties do not follow identical trends. Specifically, maximum discharge capacity and diffusion coefficient D for x = 0.20 are lower than for x = 0.16. During ball milling, nanoscale catalysts attach to Mg2Ni alloy surfaces, and catalyst size affects distribution and subsequent surface activity. As XRD patterns show, catalyst size first increases then decreases at x = 0.20, with maximum discharge capacity and D values following similar trends. This suggests catalyst crystallite size also influences catalytic effects, though specific mechanisms require further investigation.

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4 CONCLUSION

Nanosized Eu3+ and Nd3+ co-doped Ce1-x(Nd0.5Eu0.5)xO2- solid solutions were synthesized via hydrothermal method and systematically characterized for microstructure and spectral features. Ball-milled Mg2Ni-Ni-5% Ce1-x(Nd0.5Eu0.5)xO2- composites were prepared, and their electrochemical and kinetic properties were evaluated. The Ce1-x(Nd0.5Eu0.5)xO2- solid solutions exhibit fluorite cubic CeO2 phase without additional phases for x 0.20. Increasing dopant content enlarges cell parameters and volumes, increases oxygen vacancy concentration, and decreases bandgap energies. Doped solid solutions improve Mg2Ni alloy electrochemical and kinetic properties, with maximum discharge capacity increasing from 722 mAh/g (x = 0.00) to 819.7 mAh/g (x = 0.16) and cycle stability S20 improving from 25.0% (x = 0.00) to 42.2% (x = 0.20). Kinetic measurements confirm enhanced composite surface catalytic activity and hydrogen diffusion rates, particularly for x = 0.16 and x = 0.20. The catalytic mechanism, analyzed from catalyst microstructure and spectral features, identifies enlarged cell parameters, distorted lattice structure, increased oxygen vacancy content, and decreased bandgap energies as key factors optimizing electrochemical hydrogen storage properties of Mg2Ni alloys.

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Note: Figure translations are in progress. See original paper for figures.