Fast decomposition of $\text{Li}_2\text{CO}_3/\text{C}$ actuated by single-atom catalysts for Li- CO_2 batteries

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ABSTRACT Lithium carbon dioxide (Li- CO_2) batteries deliver a theoretical energy density of 1876 W h kg^{-1} in terms of effective utilization of greenhouse gases. This battery system is considered to be an encouraging electrochemical energy storage device and a promising alternative to Li-ion batteries. However, the main drawback of Li- CO_2 batteries is their accumulative discharge product of $\text{Li}_2\text{CO}_3/\text{C}$, which leads to large overpotential and poor cycling performance. Thus, specific and efficient catalysts must be explored to enhance the decomposition of $\text{Li}_2\text{CO}_3/\text{C}$. Single-atom catalysts (SACs) are regarded as promising heterogeneous catalysts owing to their maximized utilization of metal atoms and strong interfacial electronic interactions. Herein, single-metal atoms of Fe, Co, and Ni uniformly anchored on N-doped reduced graphene oxide (rGO), designated as $\text{Fe}_1/\text{N-rGO}$, $\text{Co}_1/\text{N-rGO}$, and $\text{Ni}_1/\text{N-rGO}$, respectively, are designed and fabricated to investigate their catalytic activity toward the decomposition of $\text{Li}_2\text{CO}_3/\text{C}$. Among them, $\text{Fe}_1/\text{N-rGO}$ delivers a high discharge capacity of $16,835 \text{ mA h g}^{-1}$ at 100 mA g^{-1} and maintains stability for more than 170 cycles with a discharge voltage of 2.30 V at 400 mA g^{-1} . Therefore, this catalysts are overwhelmingly superior to other types. This work reveals the advances of SACs in Li- CO_2 batteries and offers an effective method for realizing high-performance Li- CO_2 batteries.

Keywords: Li- CO_2 batteries, single-atom catalysts, $\text{Li}_2\text{CO}_3/\text{C}$, interfacial electronic interaction, M-N-C bonds

INTRODUCTION

The pursuit of high-energy density has guided the research and development of energy storage systems [1], which is exemplified by the successful commercialization of Li-ion batteries. The energy density of these batteries is twice that of Ni-Cd batteries [1,2]. However, these systems contribute to environmental pollution originating from the combustion of fossil fuels and from large

amounts of CO_2 greenhouse gas emitted into the atmosphere. To mitigate the effects of CO_2 and to maintain C neutrality, the transformation of this gas into energy is an important technology [3–4]. By effectively capturing and utilizing CO_2 [5], Li- CO_2 batteries deliver a theoretical energy density up to 1876 W h kg^{-1} [3,6], which is six times that of Li-ion batteries [1]. Therefore, Li- CO_2 batteries are considered to be encouraging devices for electrochemical energy storage and offer promising improvements over Li-ion batteries [7]. This transformation involves electrochemical reactions through reduction and regeneration of CO_2 during charge/discharge processes [4,8], such as $4\text{Li} + 3\text{CO}_2 \leftrightarrow 2\text{Li}_2\text{CO}_3 + \text{C}$ [9,10]. However, the accumulation of discharge products such as $\text{Li}_2\text{CO}_3/\text{C}$ on the surface of the catalytic cathodes is a drawback of this system [11]. The insulation characteristic of Li_2CO_3 inevitably results in inferior cycle performance and large charge overpotential [12]. Therefore, reversible formation and decomposition of $\text{Li}_2\text{CO}_3/\text{C}$ during the discharge/charge processes play an important role in improving the electrochemical performance of Li- CO_2 batteries.

During the past decade, numerous different catalysts have been fabricated to facilitate the decomposition kinetics of $\text{Li}_2\text{CO}_3/\text{C}$, including C-based materials [13–15], metals [16–18], transition metal oxides [6,19], transition metal sulfides [3,10,20], and covalent organic framework (COF) structures [21]. In particular, metal nanoparticle catalysts have proved to be effective in the decomposition of $\text{Li}_2\text{CO}_3/\text{C}$ owing to their large surface areas with high conductivity and catalytic activity. For example, Ru nanoparticles on C nanofibers (CNFs) display a low overpotential of 1.43 V after 50 cycles at 100 mA g^{-1} in Li- CO_2 batteries [22]. Jin *et al.* [23] reported that intermixed RuCu alloy nanoparticles on CNFs can work steadily for 110 cycles in Li- CO_2 batteries. Although these

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metal nanoparticle catalysts have improved the performance of Li-CO₂ batteries to some extent, the aggregation of nanoparticles and limited active sites of metal catalysts are obstacles preventing further improvement in the reversible decomposition of Li₂CO₃/C.

As heterogeneous catalysts in Li-CO₂ battery systems, metal catalysts exhibit rapid electron transfer across the catalyst/support interface and can be actuated by the particle size relevant to the interfacial electronic interaction [24]. Single-atom catalysts (SACs) reflect the ultimate small-size limit for metal nanoparticles [25]. Notably, because the size of the metal catalyst is decreased down to that of a single atom, the interfacial electronic interaction is ultimately maximized [26]. The unique chemical and physical properties of SACs, such as outstanding electronic properties, high adsorption capacity, and large surface area, facilitate the generation of new catalytic active sites and the emergence of new reaction pathways [27]. The increased under-coordination of the metal atoms in SACs contributes to the enhanced catalytic activity, and their uniform size hinders their aggregation in the support substrates. In addition, the maximized efficiency of metal atom utilization enables unique interfacial electron interaction and electron transport efficiency in SACs such as Ni, Co, and Fe [25,28], thus accelerating the kinetics of the energy-conversion reactions and boosting extraordinary catalytic activity in energy storage systems [29,30]. Li *et al.* [31] reported that the CO₂ reduction reaction (CO₂RR) is size-dependent on Ni-based catalysts and that Ni-based SACs display superior catalytic activity with a Faradaic efficiency of 97%. Zhang *et al.* [32] demonstrated that a polypropylene separator modified by SACs could effectively catalyze polysulfide conversion in Li-S batteries. In addition, they reported that Fe SACs have a capacity retention of 83.7% with remarkable cycling stability for 750 cycles, which reflects a significant improvement over other catalysts. Zhang *et al.* [33] demonstrated that Fe/N-doped graphene exhibits low reduction overpotential with a high Faradaic efficiency of 80% owing to the abundant active sites of Fe-N₄ bonds for improved CO₂ adsorption and activation. Therefore, SACs can be used as efficient catalysts in Li-CO₂ batteries to reduce polarization and to improve the charge/discharge efficiency.

In the present study, a coordination precipitation method and subsequent thermal treatment were used to fabricate three types of SACs, including single-metal atoms of Fe, Co, or Ni uniformly anchored on N-doped reduced graphene oxide (N-rGO) supports. These SACs, referred to M₁/N-rGO, where M denotes the particular

single-metal atom [32], are characterized by aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), X-ray photoelectron spectroscopy (XPS), and energy dispersive spectrometry (EDS). The electrochemical test results reveal the catalytic priority of Fe₁/N-rGO compared with that of the other two candidates. In particular, Fe₁/N-rGO delivers superior catalytic properties with a high discharge capacity of 16,835 mA h g⁻¹ and stability in more than 170 cycles with a discharge voltage of 2.30 V at 400 mA g⁻¹. The extraordinary catalytic properties of this SAC for the decomposition of Li₂CO₃/C in Li-O₂ batteries can be ascribed to the characteristics of Fe single atoms as well as their uniform dispersion on the conductive substrate of N-rGO.

EXPERIMENTAL SECTION

Synthesis of graphene oxide

The GO was synthesized using the Hummers method with modification [34]. In this process, graphite powders (1 g) were added to a mixed acid solution of H₂SO₄ (120 mL) and H₃PO₄ (13 mL) under constant stirring below 5°C. KMnO₄ (6 g) was then slowly added to the solution under continuous stirring at 50°C for 12 h, and then an oxidative H₂O₂ solution (12 mL) was added. After centrifugation, the precipitate was washed with distilled water and ethanol and subsequently freeze dried to obtain black GO powder.

Synthesis of SACs (M₁/N-rGO)

Fig. 1 illustrates the synthetic process of M₁/N-rGO. The GO was stirred and sonicated in deionized water to obtain a homogeneous dispersion, and a FeCl₃ solution was poured into the GO dispersion under sonication. After being vacuum freeze dried, the resultant three-dimensional (3D) GO-Fe foam was annealed at 750°C for 2 h under NH₃ and Ar. With simultaneous GO reduction, N-doping, and Fe atom coordination, black Fe₁/N-rGO powders were obtained. The Co₁/N-rGO and Ni₁/N-rGO were produced by using CoCl₂ and NiCl₂, respectively, as substitutes for FeCl₃. As a contrast, N-rGO was synthesized without the addition of metallic chloride.

Characterization of SACs

The crystal structures of the catalysts were examined using HAADF-STEM (JEOL ARM-200F, Tokyo, Japan), transmission electron microscopy (TEM; JEM-2100F, JEOL, Tokyo, Japan), and X-ray diffraction (XRD; D8, Bruker, Billerica, Massachusetts, United States) with Cu

Figure 1 Schematic illustration of M_1/N -rGO synthetic process.

K α radiation ($\lambda = 0.15406$ nm). The surface morphologies were characterized using scanning electron microscopy (SEM; NanoSEM 450, FEI, Hillsboro, Oregon, United States). Raman spectra were detected using a Raman microscope (InVia RM200, Renishaw, Wotton-under-Edge, Gloucestershire, United Kingdom) at an excitation wavelength of 532 nm. The interfacial electronic interaction was conducted by XPS (ESCALAB 250Xi, Thermo Scientific, Waltham, Massachusetts, United States).

Electrochemical testing

The obtained N-rGO and M_1/N -rGO catalysts and polyvinylidene fluoride (PVDF, 9:1) were ground with the addition of *N*-methyl-2-pyrrolidone (NMP) to obtain mixed slurry. The slurry was dropped onto a C paper (TEG-H-060, Toray, Tokyo, Japan) and was dried under vacuum at 120°C for 8 h. The mass loading of the electrode was about 0.3 mg cm⁻². 2032-type Li-CO₂ batteries were assembled with N-rGO and M_1/N -rGO catalysts as well as a Li plate, glass fiber separator, and electrolyte (90 μ L) of 1 mol L⁻¹ bis(trifluoromethane)sulfonimide Li salt (LiTFSI) in tetra(ethylene glycol) dimethyl ether (TEGDME) in a glove box filled with high-purity Ar with O₂ < 0.1 ppm and H₂O < 0.1 ppm. The as-assembled batteries were placed in customized and sealed chambers that were then filled with pure CO₂. To collect the discharge/charge curves, the batteries were tested with a cell tester (CT2001A Wuhan LAND Electronics Co., Ltd., Wuhan, China).

RESULTS AND DISCUSSION

The XRD patterns and Raman spectroscopy results were obtained to characterize the structures of the N-rGO and M_1/N -rGO samples. As shown in Fig. 2a, the two peaks at 26.5° and 44° are indexed to the (0 0 2) and (1 0 1) planes for graphitic C [28]. It is noteworthy that no peak is ascribed to the metal in M_1/N -rGO, revealing the absence of M–M bonds and preliminarily implying that single-metal atoms exist in the M_1/N -rGO [29,32]. The Raman

spectra shown in Fig. 2b indicate that all samples display similar C structures with a dominant D band (1350 cm⁻¹) and G band (1585 cm⁻¹) [35], further implying the atomic characteristics of metals in the M_1/N -rGO.

As a highly element-sensitive technique, XPS was performed to demonstrate the surface elemental composition and to investigate the electronic state of the metal centers in the single-metal atoms. All of the N 1s spectra in the M_1/N -rGO (Fig. 2c and Fig. S1) display three deconvoluted peaks of 398.0, 399.0, and 401.1 eV, which can be attributed to pyridinic N, pyrrolic N/M–N, and graphitic N, respectively [30,36]. These results indicate the implantation of N in the C matrix. The peaks shown in Fig. 2d at 284.8, 285.9, 287.4, and 291.5 eV are indexed to C(sp²)–C(sp²), C(sp²)–N, C(sp³)–N, and C=O, respectively, further indicating the formation of C–N bonds [37,38]. The electron transfer and CO₂ chemisorption on the N-rGO support can be facilitated by the charge-delocalized C atoms actuated by the N-dopant [13]. Additionally, high-resolution Fe 2p, Ni 2p, and Co 2p spectra are presented in Fig. 2e and Figs S2, S3, respectively. The Fe 2p spectrum exhibits six deconvoluted peaks at 708.1, 712.0, 714.8, 718.2, 722.3, and 727.3 eV (Fig. 2e). Those at 727.3 and 712.0 eV can be attributed to the Fe³⁺ species [36], with the peak at 718.2 eV reflecting the satellite peak of these species [33,36]; the other three peaks at 722.3, 714.8, and 708.1 eV can be indexed to the Fe²⁺ species [28,33]. In addition, the Ni 2p and Co 2p spectra show results similar to those of Fe 2p, revealing the formation of oxidized Fe, Ni, or Co and the interior coupling of Fe, Ni, or Co atoms on the N-rGO support (M–N–C bonds) rather than M–M bonds [39]. The successful riveting of M–N–C bonds facilitates the electron interfacial interaction of single-metal atoms and the N-rGO support [40], thus leading to substantial charge transfer across the interface [24].

The TEM and SEM images were obtained to examine the surface morphology of the Fe₁/N-rGO. As shown in Fig. 2f and Figs S4, S5, the superior transparency of Fe₁/

N-rGO indicates its thin film and the same crumpled morphology as that of N-rGO, implying the extremely small size and non-aggregation of single atoms.

Fig. 3a–d display EDS mapping images of the Fe₁/N-rGO, which demonstrate uniform distribution of the N, C, and Fe elements. Similarly, Ni and Co single atoms were uniformly supported on the N-rGO nanosheets

(Fig. S6). The HAADF-STEM analyses provide straightforward information on the size and morphology of SACs and play a crucial role in the direct imaging of catalytic centers at high-quality atomic resolution. Such images in Fig. 3e–g further demonstrate the presence of Fe single atoms. The evenly dispersed bright spots are assigned to the Fe single atoms in Fig. 3f, g. The linear STEM-EDX

Figure 2 (a) XRD pattern and (b) Raman spectra of N-rGO and M₁/N-rGO. XPS spectra of (c) N 1s, (d) C 1s, and (e) Fe 2p. (f) TEM image of Fe₁/N-rGO.

Figure 3 (a–d) EDS mapping and (e–g) HAADF-STEM images of Fe₁/N-rGO. (h) Linear STEM-EDX curve of Fe₁/N-rGO.

curve of $\text{Fe}_1/\text{N-rGO}$ shown in Fig. 3h indicates that the Fe atoms of 2–3 Å in size are isolated, and the square of the atomic number is approximately proportional to the signal intensity, which is characteristic of SACs.

The Li- CO_2 batteries were assembled to evaluate the catalytic performance of N-rGO and $\text{M}_1/\text{N-rGO}$ on the decomposition of $\text{Li}_2\text{CO}_3/\text{C}$. Fig. 4a shows the full-discharge curves of these catalysts at a current density of 100 mA g^{-1} and a cut-off voltage of 2.0 V. The $\text{Fe}_1/\text{N-rGO}$

displays the largest discharge capacity of $16,835 \text{ mA h g}^{-1}$; those of the $\text{Ni}_1/\text{N-rGO}$, $\text{Co}_1/\text{N-rGO}$, and N-rGO were 12,393, 12,134, and 9963 mA h g^{-1} , respectively. The SEM images of the four full-discharge electrodes are displayed in Fig. S7. The surface of the N-rGO catalyst is covered by large Li_2CO_3 particles of about $2 \mu\text{m}$. Compared with N-rGO, the SACs, particularly $\text{Fe}_1/\text{N-rGO}$, exhibit better electrochemical activity for the deposition of Li_2CO_3 particles with decreased size, which is beneficial to re-

Figure 4 (a) Full-discharge voltage curves of N-rGO and $\text{M}_1/\text{N-rGO}$ (M = Fe, Co, or Ni) cathodes at a current density of 100 mA g^{-1} . The first discharge/charge curves have a cut-off capacity of 1000 mA h g^{-1} at (b) 200 mA g^{-1} and (c) 400 mA g^{-1} . (d) Overpotential of N-rGO and $\text{M}_1/\text{N-rGO}$ at 200 mA g^{-1} and 400 mA g^{-1} . (e) Cycling performances of N-rGO and $\text{M}_1/\text{N-rGO}$ at 400 mA g^{-1} with a cut-off capacity of 1000 mA h g^{-1} .

ducing the charge overpotential.

The catalytic effects of single-metal atoms were further investigated at various current densities with a cut-off capacity of 1000 mA h g^{-1} . As shown in Fig. 4b, when the current density was 200 mA g^{-1} , the $\text{M}_1/\text{N-rGO}$ catalysts show similar discharge potential values of about 2.76 V, which is higher than that of N-rGO (2.50 V). These results imply that single-metal atoms can effectively reduce the discharge overpotential. Notably, the $\text{Fe}_1/\text{N-rGO}$ catalytic cathode shows the lowest charging potential, at 4.21 V. The curves presented in Fig. S8 also demonstrate the superior cycling performance of $\text{M}_1/\text{N-rGO}$ catalysts at 200 mA g^{-1} , particularly that of $\text{Fe}_1/\text{N-rGO}$, with the lowest overpotential after 80 cycles. When the current density was 400 mA g^{-1} , as shown in Fig. 4c, the discharge potential of the $\text{Fe}_1/\text{N-rGO}$ is still above 2.72 V, whereas that of the other three candidates show a reduction to a certain degree. During charging, the $\text{Fe}_1/\text{N-rGO}$ still maintains the lowest potential, at 4.33 V. Notably, it also exhibits the smallest polarization compared with that of N-rGO, $\text{Ni}_1/\text{N-rGO}$, and $\text{Co}_1/\text{N-rGO}$ (Fig. 4d).

Furthermore, at a current density of 400 mA g^{-1} , the $\text{Fe}_1/\text{N-rGO}$ was stable for more than 170 cycles with a discharge voltage of 2.30 V, a charge voltage of 4.80 V, and an increased overpotential of about 0.69 V. However, the discharge voltages of N-rGO, $\text{Co}_1/\text{N-rGO}$, and $\text{Ni}_1/\text{N-rGO}$ fell below 2.0 V after 25, 75, and 150 cycles, respectively (Fig. 4e). The discharge/charge curves of the N-rGO and $\text{M}_1/\text{N-rGO}$ catalysts are displayed in Fig. S9,

which shows much larger increases in overpotential for N-rGO, $\text{Co}_1/\text{N-rGO}$, and $\text{Ni}_1/\text{N-rGO}$. These results verify that $\text{Fe}_1/\text{N-rGO}$ exhibits extraordinary catalytic activity on the deposition and decomposition reaction of $\text{Li}_2\text{CO}_3/\text{C}$ and significantly accelerates the charge/discharge reaction kinetics owing mainly to the strong interfacial electronic interaction and high catalytic activity of SACs.

To further demonstrate the stability of $\text{Fe}_1/\text{N-rGO}$ catalysts, *ex situ* XRD and Raman characterization were performed after several cycles. As presented in Fig. 5a, the XRD patterns of discharged electrodes show new peaks at 21.2° , 30.5° , and 31.6° , which can correspond to the (1 1 0), (-2 0 2), and (0 0 2) planes of Li_2CO_3 (PDF#22-1411), respectively. The Raman spectra of discharged electrodes show a peak at 1088 cm^{-1} , also representing Li_2CO_3 (Fig. 5b). After the first charge, the characteristic peaks of Li_2CO_3 disappeared from both the XRD patterns and Raman spectra. Notably, the characteristic XRD and Raman peaks of Li_2CO_3 appeared and disappeared repeatedly before and after the 10th charging cycle. Hence, these patterns and spectra jointly illustrate the high reversibility of $\text{Li}_2\text{CO}_3/\text{C}$ decomposition. Additionally, the SEM images of the $\text{Fe}_1/\text{N-rGO}$ obtained after the first and tenth discharge/charge processes demonstrate the reversible deposition and decomposition of Li_2CO_3 particles. In contrast, after the first charge, Li_2CO_3 particles remained on the N-rGO surface (Fig. S10).

Fig. 6 illustrates the application of $\text{M}_1/\text{N-rGO}$ as fast electron transfer and catalytic cathodes for Li- CO_2 bat-

Figure 5 (a) XRD and (b) Raman spectra of the $\text{Fe}_1/\text{N-rGO}$ after different discharge and recharge processes. SEM images of $\text{Fe}_1/\text{N-rGO}$ after (c) the first discharge, (d) the first charge, (e) the tenth discharge, and (f) the tenth charge.

Figure 6 Schematic illustration of SACs applied to Li-CO₂ batteries.

teries. As a group of promising heterogeneous catalysts, M₁/N-rGO exhibits the following unique features: (1) all catalytic metal sites are anchored on the N-doped rGO support with approximately 100% usage of single-metal atoms [27]. (2) The abundant surfaces of active sites are extremely significant for facilitating CO₂ reduction and evolution reactions [41]. (3) The charge delocalization of the C atoms triggered by the N-dopant facilitates electron transfer and CO₂ chemisorption on the N-rGO support [14]. (4) The intrinsic nature of metal catalysts ensures the excellent conductivity of the SACs [40]. (5) The atomic metal sites coordinated with N and C (M–N–C bonds) further optimize the catalysis by enlarging the interfacial electronic interaction [32]. Therefore, SACs ensure abundant catalytic active sites for the decomposition of Li₂CO₃/C and rapid electron transport during catalytic reactions.

CONCLUSIONS

SACs of M₁/N-rGO have been synthesized and investigated as catalytic cathode materials for the decomposition of Li₂CO₃/C in Li-CO₂ batteries. A variety of characterizations based on HAADF-STEM, HRTEM, and EDS analyses reveal the homogenous dispersion of single-metal atoms on N-rGO. The successful riveting of strong M–N–C bonds in the M₁/N-rGO facilitates electron interfacial interaction between single-metal atoms and N-rGO supports, thus leading to the substantial charge transfer across the interface. Therefore, M₁/N-rGO catalysts exhibit high catalytic activity for the reduction of CO₂ and the decomposition of Li₂CO₃/C. Among them,

Fe₁/N-rGO exhibits the largest discharge capacity of 16,835 mA h g^{−1} and maintains stability after more than 170 cycles with a discharge voltage of 2.30 V at 400 mA g^{−1}. Our work demonstrates that SACs have strong potential in energy storage systems owing to their unique characteristics, including abundant active sites, high conductivity, strong interfacial electronic interaction, and superior catalytic activity.

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单原子催化剂促进Li-CO₂电池中Li₂CO₃/C的快速分解

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摘要 锂-二氧化碳(Li-CO₂)电池充分利用温室气体CO₂, 其理论能量密度高达1876 W h kg⁻¹, 使之被认为是未来储能系统的潜在候选者和锂离子电池的替代品. 然而, 放电产物(Li₂CO₃/C)的聚集以及缓慢的反应动力学特征, 导致其极化高、循环寿命短. 因此, 研究与开发高效催化剂来促进Li₂CO₃/C分解尤为重要. 其中, 单原子催化剂(SACs)中金属原子利用率高、界面电子相互作用强, 因而被视为有前途的多相催化剂. 本文设计合成了均匀锚定在氮掺杂还原氧化石墨烯上的单金属原子催化剂(Fe₁/N-rGO, Co₁/N-rGO和Ni₁/N-rGO), 并深入研究了它们对Li₂CO₃/C分解的催化分解活性. 其中, Fe₁/N-rGO在100 mA g⁻¹时放电比容量高达16,835 mA h g⁻¹, 且在400 mA g⁻¹时以2.30 V的放电电压稳定循环170次, 明显优于其他催化剂. 这项工作揭示了SACs在Li-CO₂电池中取得的进步, 并为实现高性能Li-CO₂电池提供了有效的方法.