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## Facile fabricate stable rare-earth bimetallic carbide as electrocatalyst for active oxygen reduction reaction

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### ABSTRACT

In this study, rare-earth bimetallic carbide  $CeLa_2C_x-NC$  has been prepared by a facile pyrolysis of o-phthalic anhydride, melamine and rare-earth elements (Ce and La). The as-prepared  $CeLa_2C_x-NC$  electrocatalyst shows satisfactory electrocatalytic activity towards oxygen reduction reaction (ORR) in alkaline electrolyte, as well as good suffering from methanol and CO poisoning, and superior stability than commercial Pt/C. It demonstrates that this rare-earth bimetallic carbide would provide a neoteric avenue for the development of ORR catalyst.

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### 1. Introduction

The cathodic oxygen reduction reaction (ORR) is the performance-limiting reaction in various electrochemical energy storage and conversion devices (such as fuel cells) [1,2]. Because the cathodic activation and decline of  $O_2$ , including  $O_2$  adsorption, O–O bond activation, and oxide removal on the electrode surface, are much more untoward than the anodic activation and oxidation of hydrogen, relatively [3,4]. In the past years, noble metal-based catalysts (Pt and Pd) are still first choice for practical application in cathode side for ORR [5,6]. However, their exorbitant cost, limited availability, low stability and suffering from methanol or CO poisoning have become bottlenecks for the large-scale manufacture of fuel cells [7,8]. As a consequence, seeking an Earth-abundant, high activity and cogent fungible for noble metal-based catalysts on ORR is extremely momentous.

Recently, metal carbides have been novel active electrocatalysts due to their electrocatalytic synergistic effect and Pt-like behavior of catalysis [9,10]. Briefly, WC [11],  $MoC_2$  [12] and  $Fe_3C$  [13] have been act as active electrocatalysts for hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and oxygen reduction re-

action (ORR), respectively. Metal carbides catalysts have the merits of eco-friendliness, low cost, high surface area and good electrical conductivity [14]. In addition, they also exhibit almost no cross effect towards methanol or CO during the catalytic process [15]. Among various metal carbides, bimetallic carbides have gained important popularity not only because of their remarkable properties like common metal carbides, but also on account of their special properties, such as their inherent stability and synergistic effect between different metals [16–18]. Bimetallic carbides like  $Co_3ZnC$  [17] and  $Co_3W_3C$  [19] have already exhibited highly active and stable for promoting noble metal-based catalysts towards ORR, which are imagined to motivate the research of bimetallic carbides. It is worth mentioning that shortly before rare-Earth metal carbide ( $CeC_x$ ) has been reported by our study [20]. But bimetallic carbides hardly ever have been studied and applied so far. More efforts are expected to acquire bimetallic carbides with excellent performance.

Herein, a rare-Earth bimetallic carbide ( $CeLa_2C_x-NC$ ) was prepared from o-phthalic anhydride, melamine and rare-Earth metals (Ce and La). Its physicochemical properties and electrochemical performance were investigated. All results certified that rare-Earth bimetallic carbide ( $CeLa_2C_x-NC$ ) has satisfactory electrocatalytic activity, good suffering from small molecules (including methanol and CO) poisoning, and superior stability than commercial Pt/C towards ORR.

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## 2. Experimental

### 2.1. Catalyst fabrication

4 g of melamine and 6 g of o-phthalic anhydride were mixed with Cerium (III) nitrate hexahydrate (0.067 g) and Lanthanum (III) nitrate hexahydrate (0.133 g), and then 100 mL of ultrapure water was added to the system. After stirring for 24 h at 60 °C, the mixture was dried at 60 °C, then transferred to a tube furnace and carbonized at 1000 °C (heating rate: 10 °C min<sup>-1</sup>) for 2 h under N<sub>2</sub> flow. Subsequently, to remove the exposed metal and metal oxide, the resultant was soaked in 0.5 M H<sub>2</sub>SO<sub>4</sub> for 24 h at ambient temperature, and then washed and dried at 60 °C. The obtained product was named as CeLa<sub>2</sub>C<sub>x</sub>-NC.

The same amount melamine and o-phthalic anhydride were mixed, and then 100 mL of ultrapure water was added to the system. Besides, the equal amount melamine and o-phthalic anhydride were mixed with Cerium (III) nitrate hexahydrate (0.2 g) or Lanthanum (III) nitrate hexahydrate (0.2 g), following the 100 mL of ultrapure water was added to the system. The detailed next procedures are as the above mentioned like CeLa<sub>2</sub>C<sub>x</sub>-NC, the obtained product was called as CeC<sub>x</sub>-NC and LaC<sub>x</sub>-NC. The mixture without adding metal was named NC. All resulting samples were ground to a fine powder for electrochemical measurement and characterization.

### 2.2. Characterization

Transmission electron microscopy (TEM) measurements were undertaken on an electron microscope (FEI TECNAI G<sup>2</sup> T20 S-TWIN TMP America). X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-2400 (Japan) diffractometer, using Cu K<sub>α</sub> radiation operated at 40 kV and 150 mA. X-ray photoelectron spectroscopy (XPS) data were performed on a Kratos Axis Ultra DLD spectrometer (Japan) with a monochromatic Al K<sub>α</sub> X-ray source ( $h\nu = 1486.6$  eV). The Raman spectra were taken with a Lab RAM HR Evolution Raman microscope (French).

The electrochemical measurements were conducted by an Autolab electrochemical work station (PGSTAT128N, Eco Chemie, Netherlands). A three electrode system was used to all electrochemical test, including an Ag/AgCl (saturated KCl) electrode as the reference, a carbon electrode as the counter and a glassy carbon (GC) rotating disk electrode (0.19625 cm<sup>-2</sup>, 5 mm in diameter) as the working electrode. To deposit the catalyst onto the GC disk electrode, 5 mg catalyst was dispersed ultrasonically in 1 mL Nafion / ethanol (0.25% Nafion). 8 μL suspensions were transferred to the surface of polished GC electrode, followed by drying in air. So the electrocatalyst amount of glassy carbon electrode is calculated as follows:  $5 \times 8 / 1000 = 0.04$  mg for all electrocatalyst. And the electrocatalyst loading is  $0.04 / 0.19625 = 0.2038$  mg cm<sup>-2</sup>. Before each measurement, the solution was purged with N<sub>2</sub> or O<sub>2</sub> gas for at least 15 min to ensure the gas saturated. All potentials mentioned in this work were measured against Ag/AgCl.

## 3. Results and discussion

### 3.1. Electrochemical discussion

To evaluate the ORR catalytic activity, linear sweep voltammograms (LSV plots) of prepared electrocatalysts were tested in 0.1 M KOH. As shown in Fig. 1a, onset potential of these electrocatalysts is in the following order: commercial Pt/C > CeLa<sub>2</sub>C<sub>x</sub>-NC > CeC<sub>x</sub>-NC > LaC<sub>x</sub>-NC > NC. The half-potential ( $E_{1/2}$ ) values of these electrocatalysts show a similar trend as the onset potential order. The  $E_{1/2}$  value of ORR on the CeLa<sub>2</sub>C<sub>x</sub>-NC electrocatalyst is approximately 15, 30, 60 mV more positive than that of the CeC<sub>x</sub>-NC, LaC<sub>x</sub>-NC

and NC electrocatalyst, respectively. These results indicate that the introduction of rare-Earth metal to the NC material significantly lessen the ORR overpotential. Obviously, the  $E_{1/2}$  value of ORR on the rare-Earth bimetallic carbide electrocatalyst is more positive and prominent than that of rare-Earth single metal carbide electrocatalysts. It could attribute to the electron-donating from rare-Earth metal carbides to NC, which favors the reduction of O<sub>2</sub> [4]. In addition, the NC has high electrical conductivity as support, which would aggrandize the affluent available active sites of electrocatalyst and boost electrons transport rapidly [21]. Through a simple evaluating, the activity of CeLa<sub>2</sub>C<sub>x</sub>-NC is worth expecting and the other electrocatalytic performances were further assessed.

The electrocatalytic activity of CeLa<sub>2</sub>C<sub>x</sub>-NC electrocatalyst towards ORR was examined by cyclic voltammetric (CV) measurements in N<sub>2</sub> and O<sub>2</sub>-saturated 0.1 M KOH aqueous solutions with a scan rate of 50 mV s<sup>-1</sup>. As presented in Fig. 1b, for CeLa<sub>2</sub>C<sub>x</sub>-NC electrocatalyst, in N<sub>2</sub>-saturated electrolyte, the CV curve exhibit a quasi-rectangular voltammogram without apparent peaks within the potential range -1.0 to +0.2 V. In sharp contrast, in the case of O<sub>2</sub>-saturated electrolyte, CeLa<sub>2</sub>C<sub>x</sub>-NC electrocatalyst shows a substantial reduction process with a noticeable reduction peak (located at -0.285 V). These results suggest that both bimetallic carbide and N-doped carbon have effects on improving the ORR catalytic activity for CeLa<sub>2</sub>C<sub>x</sub>-NC in alkaline media. The well catalytic performance possibly rests on carbon sheet, it serves as conductor for efficient electron transportation and restrains bimetallic carbide nanoparticles from agglomeration [22]. Cycle stability should be importantly taken into consideration for cathode materials towards practical application in fuel cells [23]. The stability of the CeLa<sub>2</sub>C<sub>x</sub>-NC electrocatalyst was evaluated using an accelerated durability test by potential cycling within a range of -0.8 ~ 0.2 V in O<sub>2</sub>-saturated electrolyte. After 1000 cycles, the  $E_{1/2}$  potential of CeLa<sub>2</sub>C<sub>x</sub>-NC in KOH solution have negatively shifted by 1.6 mV (Fig. 1d), which is smaller than that of commercial Pt/C (18.8 mV, Fig. 1c). The changes of  $E_{1/2}$  potential during the cycling tests manifest that the CeLa<sub>2</sub>C<sub>x</sub>-NC electrocatalyst has better durability than commercial Pt/C electrocatalyst. Many reports have demonstrated that the carbides could induce the molecular charge transfer, this result make electrocatalysts have better long-term operation stability than that of commercial Pt/C electrocatalyst [24]. Probably, the Pt/C generally suffers from the particle aggregation and dissolution to reduce the surface area, resulting in declined activity and limiting current in stability test [25]. Meanwhile, the CeLa<sub>2</sub>C<sub>x</sub>-NC electrocatalyst is very stable without the probable to aggregate or decline the activity.

The crossover effect and superb stability should be considered as well due to small organic fuel molecules, such as methanol, may pass through the electrolyte membrane from anode to cathode and seriously compromise the active of entire fuel cell [2,26]. So the ORR polarization curves were tested for commercial Pt/C and CeLa<sub>2</sub>C<sub>x</sub>-NC electrocatalysts in 0.1 M KOH with 0.5 M CH<sub>3</sub>OH under O<sub>2</sub>-saturated at a scan rate of 5 mV s<sup>-1</sup>. From Fig. 2a, commercial Pt/C electrocatalyst appears distinct mixed potential, and an oxidation of methanol current peak is exhibited at -0.17 V (vs. Ag / AgCl). By comparison, CeLa<sub>2</sub>C<sub>x</sub>-NC electrocatalyst has no obvious oxidation of methanol peak. These results confirm the poor tolerance to methanol of commercial Pt/C and excellent resistance to crossover effects of the CeLa<sub>2</sub>C<sub>x</sub>-NC. The result of this will be further verified in the next current-time (i-t) test with adding methanol solution. Subsequently, the stability, methanol crossover and CO poisoning were further assessed on both CeLa<sub>2</sub>C<sub>x</sub>-NC and commercial Pt/C electrocatalysts at -0.3 V in O<sub>2</sub>-saturated 0.1 M KOH solution [27]. As presented in Fig. 2b, for CeLa<sub>2</sub>C<sub>x</sub>-NC electrocatalyst, the catalytic current density only show a subtle declination after injecting 3 M methanol, while commercial Pt/C electrocatalyst appear a sharp transform in current density. This

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