

# The SeCN<sup>-</sup> Ions-Decorated Cobalt Selenide Catalyst for Oxygen Reduction Reaction and Application in Alkaline Fuel Cell

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## Abstract

The specific morphology of cobalt diselenide was synthesized to be a transition metal active center. Then mixing with carbon and nitrogen precursors and go through the pyrolysis procedure at a sufficient temperature. Later, this non-precious metal catalyst was denoted as CoSe/SC. It generated an excellent Oxygen Reduction Reaction (ORR) ability with the electron-transfer number of 3.994, which is very close to the ideal four electron-transfer numbers.

The high catalytic performance of the CoSe/SC is attributed to the SeCN<sup>-</sup> bonding within the structure by using XAS, XPS and FT-IR analysis, so that it can promote the kinetic current and electron transfer. The other reason is the peak located at 396.3eV, which corresponded to Co-N bond and playing the active sites for ORR from NEXAFS N K-edge. These characteristics boosted the active sites and reactivity during the ORR.

Eventually, it showed the outstanding Anion Alkaline Exchange Membrane Fuel Cell (AAEMFC) performance closed to 150 mW cm<sup>-2</sup> which demonstrated the better power performance than other non-precious metal catalysts.

## 1. Introduction

Hydrogen energy is a popular application recently; people are following this direction for alternative energy sources. The anion exchange membrane fuel cell (AEMFC) is one of the fuel cells applications, and it's an electrochemical power source that transforms chemical energy into electrical energy efficiently. Recently, Mukerjee et al. showed that the non-precious metal catalyst has better ORR activity in the alkaline environment than in the acidic environment and also promoted the ORR mechanism[1]. The primary advantage of performing ORR in alkaline media is found to be the enhanced activation of the peroxide intermediate that enables the complete four-electron transfer. This evidence opens the possibility of using a wide-range of non-noble metal surfaces as electrode materials for the ORR in alkaline media.

## 2. General Instructions

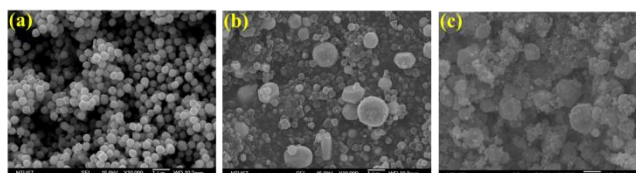
### 2.1 Experimental setup-Preparation of CoSe/SC

The 55 wt% of Co(C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub> (99% purity, Acros) was put into the Teflon can, then mixing with 12.5 wt% oleic acid (90% purity, Aldrich) and 87.5 wt% anisole (99% purity, Acros). After stirring for 30 minutes, 35 wt% of Sele-

nium powder (99.5% purity, Acros) and 10 wt% of N/C (Urea mixed with carbon) were added into. The above Teflon can follow by using the hydrothermal muffle treatment in sufficient temperature and holding time. Then, the mixtures were introduced into a horizontal tubular quartz reactor in the furnace. The pyrolysis was conducted in an Argon atmosphere, with a ramping-up rate of 20 °C min<sup>-1</sup>, and fixed at suitable temperatures for 2 h. Subsequently, the furnace was naturally cooled to room temperature overnight.

### 2.2 Results and discussion

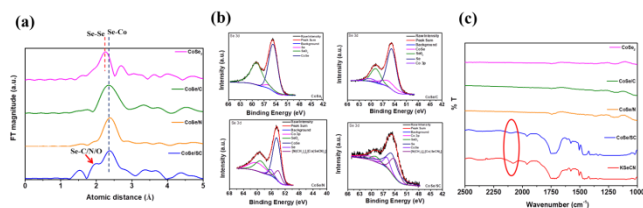
The special morphology CoSe<sub>2</sub> was synthesized in a suitable precursor, surfactant and solvent ratio. Then go through the hydrothermal muffle furnace and fixed at a specific temperature and holding time. Finally, the pearl-like CoSe<sub>2</sub> was uniformly and got particle size around 450-500 nm as shown in **Figure 1(a)**. The after-pyrolysis CoSe<sub>2</sub> and CoSe/SC were observed in **Figure 1 (b), (c)**, respectively. It indicated that the morphology was been destroyed and the new chemical bonding produced during the heat treatment.



**Figure 1** The SEM image of (a) pearl-like CoSe<sub>2</sub>; (b) pearl-like CoSe<sub>2</sub> after-pyrolysis; (c) CoSe/SC nanoparticles.

**Figure 2 (a)** clarified the EXAFS spectra at the Se K edge for CoSe<sub>2</sub>, CoSe/C, CoSe/N, and CoSe/SC nanoparticles. It's worth noting that only CoSe/SC had the specific peak at 1.96 Å in the spectrum which might associate with Se-C/N/O. This assumption would go through the XPS, FT-IR measurement and shown in **Figure 2 (b), (c)**. The Se 3d orbital spectra of all samples could be fitted into several chemical states at specific binding energies, as shown in **Table 1**. It was noteworthy that the sample which concluded the nitrogen precursor showed the chemical compound [N(CH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>[Co(SeCN)<sub>4</sub>] at 54.1 eV [2]. In the case of CoSe/SC, related to the highest content of the specific composition. On the basis of the above structural characterizations, it seemed that selenocyanate ion was relied on the assumption of critical properties for ORR to promote the activity. All samples were measured and compared to the

commercial Potassium Selenocyanate (KSeCN), as shown in **Figure 2 (c)**. The fundamental CN stretching appeared at  $2070\text{ cm}^{-1}$  which could be generate to the  $\text{SeCN}^-$  ions[3]. It could be distinctly seen that the same vibration in the CN frequencies followed a similar pattern in the best parameter CoSe/SC and commercial one. Selenocyanate ion ( $\text{SeCN}^-$ ) was a kind of pseudo halogen ions with highly redox potential and simple internal redox kinetics results in faster electron transfer [4]. Owing to the above properties, selenocyanate ion was largely been applied to the dye-sensitized solar cells [4, 5].



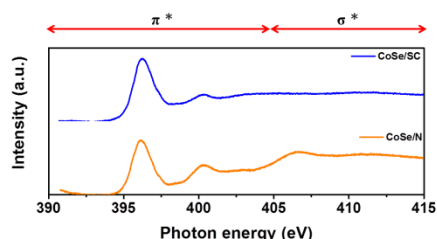
**Figure 2** The (a) EXAFS for Se K-edge spectra; (b) XPS Se 3d spectra; (c) FT-IR spectrum for CoSe<sub>2</sub>, CoSe/C, CoSe/N, CoSe/SC.

**Table 1**

The fitting results from XPS analysis for Se 3d spectra.

Structure/ Sample	Co3p	SeO <sub>2</sub>	Se	CoSe	[N(CH <sub>3</sub> ) <sub>4</sub> ] <sub>2</sub> [Co(SeCN) <sub>4</sub> ]
B.E.(eV)	60.3	58.9	56	54.6	54.1
CoSe <sub>2</sub>	0%	42%	5%	53%	0%
CoSe/C	5%	21%	15%	59%	0%
CoSe/N	19%	20%	6%	45%	10%
CoSe/SC	14%	7%	12%	45%	22%

**Figure 3** showed the XAS spectra at the N K absorption edge of sample CoSe/SC and CoSe/N measured at 300 K. The first adsorption peak at 396 eV arise from the optical transition from N 1s to unoccupied N 4p orbital strongly hybridized with Co(II) 3d minority spin state[6]. Thus, after cobalt bonding with nitrogen, more empty orbitals would be provide by metal and more electrons would be attract because of nitrogen which with the high electronegativity. The second peak which located at 400.2 eV was attributed to the splitting of  $\pi^*$ -resonance arises from conjugation effects for the imine nitrogen (C=N) [7]. A conjugated system had a region of overlapping p-orbitals, bridging the interject single bonds. These allowed a delocalization of  $\pi$  electrons across all the adjacent aligned p-orbitals. The  $\pi$  electrons did not belong to a single bond or atom, but rather to a group of atoms.



**Figure 3** NEXAFS for CoSe/SC, CoSe/N from N K-edge spectra.

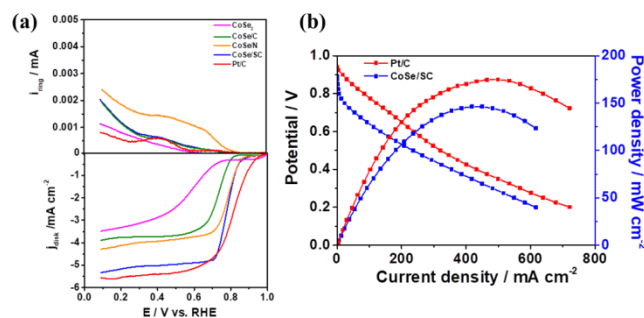
**Figure 4 (a)** showed the comparative ORR activity of CoSe/SC and commercial Pt/C. The lower part of the figure plots the disk current ( $I_d$ ) against the applied potential and the upper part plots the ring current ( $I_r$ ) as a function of the applied potential. In particular, the CoSe/SC showed the best kinetic current of  $I_d$

$$n = \frac{4I_d}{I_d + \frac{I_r}{N}}, \quad (1)$$

$$\%HO_2^- = \frac{2I_r}{I_d + \frac{I_r}{N}} \times 100\%, \quad (2)$$

Where N, denotes the RRDE collection efficiency, was determined to be 0.368.

**Figure 4 (b)** showed the single cell test performance which through the operating temperature  $60^\circ\text{C}$ , 100% humidity and proper gas flow rate. The non-precious metal catalyst N-CoSe<sub>2</sub>/C which made in a simple method presented the power density around  $150\text{ mW cm}^{-2}$  that better than others, and very close to the best catalyst commercial Pt/C.



**Figure 4** The (a) ORR activity curve and (b) single cell test performance.

### 3. Conclusions

- 1). The CoSe/SC catalyst demonstrated the excellent ORR activity and outstanding electron transfer number.
- 2). The high ORR activities and excellent full cell performance could be ascribed to the  $\text{SeCN}^-$  ions with highly redox potential and the unoccupied N 4p orbital strongly hybridized with Cobalt (II) from series of material analysis.

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### References

- [1] Y. Feng, N. Alonso-Vante, *Electrochimica Acta*, 72 (2012) 129-133.
- [2] J. Escard, G. Mavel, J.E. Guerschais, R. Kergoat, *Inorganic Chemistry*, 13 (1974) 695-701.
- [3] F.A. Cotton, D.M.L. Goodgame, M. Goodgame, T.E. Haas, *Inorganic Chemistry*, 1 (1962) 565-572.
- [4] Y.-F. Lin, C.-T. Li, C.-P. Lee, Y.-A. Leu, Y. Ezhumalai, R. Vittal, M.-C. Chen, J.-J. Lin, K.-C. Ho, *ACS Applied Materials and Interfaces*, 8 (2016) 15267-15278.
- [5] A. Solangi, A.M. Bond, I. Bugar, A.F. Hollenkamp, M.D. Horne, T. Ruther, C. Zhao, *Journal of Physical Chemistry B*, 115 (2011) 6843-6852.
- [6] K.H. Keita Ito, Kaoru Toko, Mao Ye, Akio Kimura, Yuki Haru Takeda, Yuji Saitoh, Hiro Akinaga, Takashi Suemasu, *Applied Physics Letters*, 99 (2011) 1-3.
- [7] L. G. Bulusheva\*, E. O. Fedorovskaya1, A. V. Okotrub1, E. A. Maximovskiy1, D. V. Vyalikh2, Xiaohong Chen3, and Huaihe Song3, *Phys. Status Solidi B*, DOI (2011) 2484-2487.