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# Hydrothermal Synthesis, Structure Refinement, and Electrochemical Characterization of Li<sub>2</sub>CoGeO<sub>4</sub> as an Oxygen Evolution Catalyst

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Lithium cobalt germanate (Li<sub>2</sub>CoGeO<sub>4</sub>) has been synthesized for the first time by a hydrothermal method at 150 °C. Elemental composition, morphology, and crystal structure of this compound were characterized by various analytical techniques including SEM, TEM, ICP, and XRD analyses. Structure refinement and DFT calculation suggests the crystal structure of the resulting Li<sub>2</sub>CoGeO<sub>4</sub> from hydrothermal synthesis is isostructural to Li<sub>2</sub>ZnGeO<sub>4</sub>, significantly different from previous reports. Electrochemical studies confirmed Li<sub>2</sub>CoGeO<sub>4</sub> as an active catalyst for oxygen evolution reaction (OER). In alkaline electrolyte (0.1 M NaOH), rotating disk electrodes made with Li<sub>2</sub>CoGeO<sub>4</sub> as catalyst have a Tafel slope of c.a. 67 mV/dec and an overpotential of 330 mV at 50  $\mu$ A/cm<sup>2</sup><sub>cat</sub>, about 90 mV less than the electrodes containing another known OER catalyst, Co<sub>3</sub>O<sub>4</sub>. Further characterization with cyclic voltammetry, high resolution transmission electron microscopy, X-ray photoelectron spectroscopy and elemental analyses revealed the oxidation of Co from 2+ to 3+ during the reaction along with significant surface amorphization and loss of Li and Ge from the catalyst.

## Introduction

Water splitting and artificial photosynthesis systems are currently under intensified study for the conversion and storage of solar energy into chemical fuels.<sup>1-7</sup> However, the efficiency of those processes is often limited by the sluggish kinetics of the four proton-coupled electron transfers required for the oxygen evolution reaction (OER).<sup>8</sup> IrO<sub>2</sub> and RuO<sub>2</sub> are known catalysts that can effectively reduce activation barriers for OER, but their material cost is too high. Therefore, it is still essential to find low-cost catalyst alternatives that are feasible for large scale applications, such as those targeting to reduce atmospheric CO<sub>2</sub> level and remediate the risk of global climate change.<sup>3</sup>

Among the many recent efforts focusing on oxide-based materials, there has been a growing interest to examine lithium containing oxides, previously known as cathode materials of lithium ion batteries, for use as OER catalysts. Recently,  $LiCoO_2$  and  $LiCoPO_4$  were studied thoroughly for OER catalysis in both alkaline and neutral electrolytes.<sup>9</sup> A combination of structural and electrochemical analyses revealed the important role of catalyst surface properties to their activities. Likewise,  $LiMn_{1.5}Ni_{0.5}O_4$  was used to systematically investigate the effect of surface planes/facets on OER activity and it has been found that catalyst activity increased in the order of truncated octahedral < cubic < spherical < octahedral surface structures.<sup>10</sup> More recently, a new catalyst based on lithium manganese pyrophosphate was studied for water

oxidation at neutral pH, from which the role of Mn valency in OER catalysis was elucidated via controlled delithiation ( $Li_{2-x}MnP_2O_7$ , x=0, 0.3, 0.5, 1).<sup>11</sup>

 $Li_2CoGeO_4$  (LCG) belongs to the same family of compounds as  $Li_2CoSiO_4$  (LCS) with structure derived from  $Li_3PO_4$ . Recently the synthesis, crystal structure, and electrochemical properties of LCS were extensively investigated for lithium ion battery application.<sup>12-15</sup> However, for LCG, there has been no dedicated study, except for a few very old reports.<sup>16-19</sup> Herein, we report for the first time hydrothermal synthesis of  $Li_2CoGeO_4$ , as well as the characterization of its material properties and use as OER catalyst. Structural refinement and DFT calculation were also conducted to clarify the ambiguity on its crystal structure from previous studies.

## Experimental

**Materials synthesis.** LCG was prepared by hydrothermal synthesis from GeO<sub>2</sub> (Sigma-Aldrich), LiOH·H<sub>2</sub>O (Sigma-Aldrich), and CoCl<sub>2</sub>·6H<sub>2</sub>O (Sigma-Aldrich). Into an 80 mL Teflon lined autoclave 0.0125 mol of GeO<sub>2</sub> and 0.05 mol of LiOH·H<sub>2</sub>O were added to 20 mL of deionized water. In a separate beaker 0.0125 mol of CoCl<sub>2</sub>·6H<sub>2</sub>O was dissolved in a mixture of ethylene glycol (10 ml) and H<sub>2</sub>O (10 ml), and then added to 150 °C for 12 h. The resulting product was

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filtered, washed with deionized water, and dried under vacuum (60 °C, 12 h). After drying, the powder was ground using a mortar and pestle then used for characterization.

Characterization of materials properties. Morphology of hydrothermal synthesized LCG (hydro-LCG) was studied on a JEOL 7800 field emission scanning electronic microscope (SEM) and JEOL 3011 high resolution transmission electronic microscope (HR-TEM). Elemental composition was determined by inductively coupled plasma (ICP, Evan Analytical) analyses. The structure of the samples was characterized by powder X-ray diffraction (XRD), using a Rigaku Smart Lab θ-θ powder diffractometer equipped with a Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å) source. The data was collected with a step size of 0.02° and exposure time of 12 s. Rietveld refinement of the powder XRD patterns was performed using the GSAS/EXPGUI package.<sup>20</sup> X-ray photoelectron spectroscopy (XPS) analysis was conducted on a PHI 5000 VersaProbe II system to verify the valance state of Co for hydro-LCG and Co<sub>3</sub>O<sub>4</sub>. High resolution Co 2p scans were performed with 23.5 eV pass energy and a scan step of 0.1 eV. Specific surface area of hydro-LCG was measure by nitrogen adsorption and desorption (BET) using a Micromeritics ASAP 2020 Surface Area and Porosity Analyser.

Electrode Preparation and Electrochemical Measurements. Electrochemical experiments were performed in 0.1 M NaOH solution at room temperature in three electrode cells using a VSP multichannel potentiostat (Bio-logic). Working electrodes for cyclic voltammetry (CV), galvanostatic and Tafel analyses were prepared using a previously reported procedure.<sup>21,22</sup> A catalyst ink was first prepared by sonicating a mixture of catalyst, acid-treated carbon black (CB, Alfa Aesar), Na+exchanged Nafion® solution (5 wt%, Ion Power) with tetrahydofuran (THF, Sigma-Aldrich), and then drop-cast (10 µL) onto pre-polished glassy carbon disk electrodes (5 mm in diameter, Pine Instruments). The catalyst film was allowed to dry at room temperature overnight and the final composition of the film was expected to be 100, 20, and 20  $\mu$ g/cm<sup>2</sup> for hydro-LCG, CB, and Nafion®, respectively. Working electrodes rotated at 1600 rpm using a rotating disc electrode system (Pine Instruments). The counter electrode was a Pt coil isolated from the main electrochemical cell using a fritted glass tube. All potentials were measured versus a Ag/AgCl (4 M KCl) reference electrode, corrected for IR drop, and converted to reversible hydrogen electrode (RHE) for easy discussion and comparison to previous literature. Electrodes for XPS, HR-TEM and SEM EDX analyses were prepared by depositing hydro-LCG particles directly on Indium Tin Oxide (ITO) coated glass slides (10x45 mm, LGA) via dip coating from a catalyst suspension in ethanol (1.0 mg/ml). To confirm O<sub>2</sub> product and estimate Faraday efficiency, bulk electrolysis was performed with a hydro-LCG/ITO electrode in a two-chamber air-tight electrochemical cell. An optical O2 sensor (Ocean optics, Foxy-R) was used to monitor O<sub>2</sub> concentration in the headspace of the anode chamber, from which the total amount of O<sub>2</sub> product was estimated via Henry's law.

**DFT calculations.** DFT calculations were performed with the Vienna *ab initio* Simulation Package (VASP) used projector augmented waves (PAW) pseudopotentials and the exchange-correlation functionals parameterized by Perdew, Burke, and Ernzerhof for the generalized gradient approximation (GGA). <sup>23-26</sup> A cutoff energy of 500.0 eV was used to ensure numerical

Journal Name convergence to less than 5 meV per LCG formula. The Gamma centered k-point mesh was sampled with the density of at least  $0.03 \text{ Å}^{-1}$ . GGA+U method was used to treat the static correlations by introducing a Hubbard type potential to describe the d-part of the Hamiltonian. The value of effective U (U-J) is set to be 5.7 eV as suggested in previous reports for Co.<sup>27</sup> After the crystal structure is relaxed, powder X-ray diffraction pattern is simulated with Mercury code.

## **Results and discussion**

Previous report of synthesizing LCG used high temperature solid state process, involving an initial heating of the mixture of Li<sub>2</sub>CO<sub>3</sub>, CoO, and GeO<sub>2</sub> at 700 °C for ~2-3 h and then subsequent overnight sintering at 1000 °C to complete the reaction.<sup>16</sup> In an attempt to use more mild synthesis conditions, LCG in this work was prepared via a hydrothermal method for the first time, by heating reaction precursors (stoichiometric amount of CoCl<sub>2</sub> and GeO<sub>2</sub> with excess LiOH) in an ethylene glycol/water solution at 150 °C for 12 h. Figure 1 shows SEM and TEM images of the resulting hydro-LCG product. SEM images of the hydro-LCG powder (Figure 1(a,b)) consists of particles with a flower-like morphology with size in the range of a few hundred nanometers. It can be seen from the TEM image (Figure 1(c)) that each individual particle is composed of smaller triangular shaped petals. High resolution-TEM images along with the electron diffraction pattern confirmed that these triangular petals are highly crystalline (Figure 1(d)).



**Figure 1.** Morphology of hydrothermally synthesized hydro-LCG: (a, b) SEM images of the powder sample, (c) TEM image of a selected triangular petal and (d) high resolution TEM image showing the crystal lattice and electron diffraction patterns (insert).

 $Li_2MXO_4$  has a large family of structures comprised of distorted hexagonal close packing oxygen ions with half of the tetrahedral sites occupied by cations (Li, M, and X). To the best of our knowledge, the crystal structure of LCG has only been discussed in three publications. Glasser et al. reported the polymorph  $\gamma_{II}$  structure with space group Pnma (PDF 04-002-

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4634),<sup>18</sup> and Tarte et al. assigned their structure to the  $\beta_{II}$  polymorph, space group Pmn2/1 (PDF 04-001-8430),<sup>19</sup> whereas West et al. proposed that the structure of LCG could be orthorhombic but did not assign any space group.<sup>17</sup> However, the XRD pattern obtained from hydro-LCG in this study, as shown in Figure 2, cannot be indexed to any of the previously reported crystal structures. ICP analysis confirmed the Li:Co:Ge ratio of hydro-LCG was 2:1:1 eliminating the possibility of a non-stoichiometric cation composition that may create structural differences. Therefore, we postulate hydro-LCG may have a different crystal structure from those reported previously.



**Figure 2.** (a) Refined powder x-ray diffraction pattern for hydro-LCG, space group  $P_n$  (7). (b) Schematic visualization of hydro-LCG crystal structure in the (left) [001] and (right) [010] directions. Li, Co, and Ge tetrahedral with connecting oxygen atoms (red circles) are represented by green, blue, and yellow colour, respectively.

In order to shed light on the structure analysis, Rietveld refinements were performed using the reported LCG models ( $\beta_{II}$  and  $\gamma_{II}$ ). Additionally, two other well-known structure models based on LCS ( $\beta_{I}$ , space group Pbn2<sub>1</sub> and  $\gamma_{0}$  space group P2<sub>1</sub>/n), an isoelectronic compound to LCG, were examined by substituting Ge<sup>4+</sup> for Si<sup>4+, 15</sup> After refinement the

 $\beta_I$ ,  $\beta_{II}$ , and  $\gamma_{II}$  models led to unacceptable results with the  $R_p$  and  $R_{wp}$  typically larger than 15% and 25%, respectively (ESI S1). The  $\gamma_{II}$  polymorph was unable to generate any results likely due to a large difference in structure.

Although the LCS and LCG structures are isoelectronic with one another, the size discrepancy between Si<sup>4+</sup> (0.26 Å) and Ge<sup>4+</sup> (0.39 Å) could lead to large differences in refinement between the different polymorphs of LCS and hydro-LCG.<sup>28</sup> To determine if this was the case, additional refinements were conducted by isoelectronically substituting two ions closer in size Co<sup>2+</sup> (0.58 Å) for Zn<sup>2+</sup> (0.60 Å) in a Li<sub>2</sub>ZnGeO<sub>4</sub> (LZG) model system (Space group P<sub>n</sub> (7)) (PDF#04-015-4929).<sup>29</sup> The Rietveld refinement of the hydro-LCG diffraction pattern, using starting coordinates from LZG structure, gave acceptable fitting results, as shown in Figure 2. Table 1 summarizes refined crystallographic parameters for hydro-LCG.



**Figure 3.** (a) XRD patterns of LCG in the range of 15-45° two theta: (i) measured experimentally, as well as simulated using (ii) LZG, (iii)  $\beta_{I}$ , (iv)  $\beta_{II}$ , (v)  $\gamma_{o}$ , and (vi)  $\gamma_{II}$ . (b) Enhanced view between 15-25° two theta of (i) experimentally prepared and (ii) LZG simulated LCG showing the presence of weak peaks near 16° and 24° for both patterns. Full range patterns can be found in ESI S2.

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atom	а	b	С	Occupancy	U <sub>iso</sub>
Lil	0.4461	0.1495	-0.06567	1	0.01531
Li2	0.9317	0.2828	0.3756	1	0.04831
Co	0.2277	0.3281	0.4813	1	0.01889
Ge	-0.01900	0.1872	-0.03759	1	0.05976
01	0.8300	0.36075	0.4072	1	0.0956
02	0.2049	0.6774	0.3800	1	0.00210
O3	1.0014	-0.1522	0.5077	1	0.02680
O4	0.1681	0.2875	0.9073	1	0.00917
					2

 $* R_{p} = 7.58\%, Rwp = 9.94\%, a = 6.3505(9) \text{ Å}, b = 5.4745(3) \text{ Å}, c = 5.0062(5) \text{ Å}, V = 174.049(9) \text{ Å}^{3}, \beta = 90.218, \rho_{calc} = 4.039 \text{ g/cm}^{3}, \rho_{calc} = 4.039 \text{ g/cm}^{3}, \rho_{calc} = 4.039 \text{ g/cm}^{3}, \rho_{calc} = 4.0$ 

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In order to further verify the crystal structure for hydro-LCG, DFT relaxations were performed with five structure models, including the earlier mentioned  $\beta_I$ ,  $\beta_{II}$ ,  $\gamma_0$ ,  $\gamma_{II}$ , and LZG. The fully relaxed structures were used to simulate the powder X-ray diffraction pattern. Figure 3 shows the X-ray diffraction pattern of hydro-LCG collected experimentally compared to the simulated ones. Several characteristic differences were observed. First, the structure relaxed with LZG model showed minimum peak intensity around 16°, while all the others showed diffraction peaks with considerable intensity at the same range. The experimental pattern showed a weak peak at 15.9°, which was only consistent with the LZG model (Figure 3b). Second, the experimental pattern showed three diffraction peaks between 20-25°, with two peaks at 21.2° and 22.3° at similar intensity and the third peak with much lower intensity at 23.7°. This characteristic was obviously only captured by the LZG model, while in all the other models the intensities of these peaks were in different ratios. Third, at 32° there was only one single peak on the experimental pattern, which again agrees the best only with the LZG model. The peak splitting at this range was noticed in all other models. These characteristics strongly support the conclusion that hydro-LCG is actually isostructural to LZG. Interestingly, the calculated energy was also the lowest for LZG model, although the energy difference was not huge (30-240 meV per formula, see ESI S3 for details).



**Figure 4.** Comparison of hydro-LCG and  $\text{Co}_3\text{O}_4$  as OER catalysts in 0.1 M NaOH. (a) LSVs measured at 1 mV s<sup>-1</sup>; (b) galvanostatic measurements at 50  $\mu$ A/cm<sup>2</sup><sub>cat</sub>; (c) steady-state Tafel plots based on the average of three independent measurements (labeled with  $\Delta$ ,  $\circ$  and  $\diamond$ , respectively). Catalyst loading: 0.1 mg/cm<sup>2</sup><sub>geo</sub>; Current density was normalized based on specific surface area of the catalysts, 23.0 and 45.1 m<sup>2</sup>/g, for hydro-LCG, Co<sub>3</sub>O<sub>4</sub>, and carbon black (control, 77.0 m<sup>2</sup>/g), respectively. Solution ionic resistances were compensated at ~55 and ~60  $\Omega$  for hydro-LCG and Co<sub>3</sub>O<sub>4</sub> RDEs, respectively. (d) O<sub>2</sub> evolution from a dip coated hydro-LCG/ITO electrode at 1.63 V (vs. RHE), applied from 30 to 90 min. The O<sub>2</sub> product was measure by an optical O<sub>2</sub> sensor. Theoretical value was calculated based on the accumulated charges transferred through the working electrode.

Hydro-LCG is a potential catalyst for OER similar to other lithium cobalt compounds.<sup>9</sup> To assess its activity, hydro-LCG

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was deposited on glassy carbon rotating disk electrodes (RDEs) by drop-casting as catalyst/carbon black/Nafion composite thin films. Electrodes containing commercially purchased Co<sub>3</sub>O<sub>4</sub> nanoparticles, another known OER catalyst, were also prepared and tested using the same procedure for comparison purposes. All electrochemical characterizations were conducted in alkaline electrolyte (0.1 M NaOH) saturated with oxygen. Linear sweep voltammograms (LSVs) at a scan rate of 1 mV s<sup>-1</sup> on electrodes with and without catalysts are shown in Figure 4 (a). Catalytic activity of hydro-LCG and Co<sub>3</sub>O<sub>4</sub> is evident as a significant increase in current at potentials more positive than 1.55 V was observed for both catalysts compared to a control electrode without catalyst. It can be seen that hydro-LCG has an earlier onset for water oxidation and is able to achieve higher currents as the applied positive potential increases. Such a higher activity of hydro-LCG is further confirmed with galvanolstatic analysis. At a constant current of 50  $\mu$ A/cm<sup>2</sup><sub>cat</sub>, an overpotential of 330 mV (1.56 V vs. RHE) for OER was observed from hydro-LCG electrodes, as compared to 420 mV (1.65 V vs. RHE) from  $Co_3O_4$  (Figure 4(b)). Figure 4(c) shows Tafel plots of the two catalysts obtained under steady state conditions. Tafel slopes, determined from the average of three independent tests, are calculated as 67 and 66 mV/dec, for hydro-LCG and Co<sub>3</sub>O<sub>4</sub>, respectively, similar to those reported on LiCoO<sub>2</sub> and LiCoPO<sub>4</sub>.<sup>9</sup> Remarkably, the exchange current density from hydro-LCG electrode was estimated as 5.6x10<sup>-10</sup> A/cm<sup>2</sup><sub>cat</sub>, about one order of magnitude higher than that of  $Co_3O_4$  (4.3x10<sup>-11</sup> A/cm<sup>2</sup><sub>cat</sub>). To verify  $O_2$  production, bulk electrolysis was conducted in an air-tight, 2-chamber electrochemical cell equipped with an optical O<sub>2</sub> sensor. As shown in Figure 4(d), once the applied potential was switched on (at 30 min), the generation of O<sub>2</sub> product was evident, and the Faraday's efficiency is estimated as ~90%.



**Figure 5.** Cyclic voltammagrams at a 1 mVs<sup>-1</sup> scan rate for (a) hydro-LCG and (b)  $Co_3O_4$  as well as a 10 mVs<sup>-1</sup> scan rate for (c) hydro-LCG and (d)  $Co_3O_4$  in 0.1 M NaOH. Data are plotted at different scale to better visualize the redox waves. Please refer to ESI S4 for comparison at same scale.

LSV of hydro-LCG shows a characteristic oxidation peak around 1.41 V vs. RHE prior to OER current, which was also

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seen as a redox couple from cyclic voltammetry (CV) analysis (Figure 5(a)). Such a transition very likely corresponds to  $Co^{2+}/Co^{3+}$  oxidation, as reported from many Co-containing OER catalysts.<sup>32, 33</sup> The  $E_{1/2}$  of this redox couple is 1.43 V at first CV cycle and downshifted to ~1.20 V at the 2<sup>nd</sup> cycle and thereafter. Similar pre-OER redox peaks were also observed from Co<sub>3</sub>O<sub>4</sub> (Figure 5(b)), but they were at higher potentials and appeared to be stable during the CV cycles. It is unclear if the lower redox potential as observed from hydro-LCG contributes to its high activity, which remains a subject for future study.



**Figure 6.** SEM (left column) and HR-TEM (right column) images of dip coated pristine (a) and hydro-LCG on ITO electrodes after one (b) and one hundred (c) CV cycles. Inserts: fast Fourier transform (FFT) of catalyst surface regions. Scan rate:  $10 \text{ mV} \cdot \text{s}^{-1}$ .

Under galvanostatic condition (Figure 4(b)), the potential of both hydro-LCG and Co<sub>3</sub>O<sub>4</sub> electrodes increased at the beginning and then became steady towards the end of the test. Stability of the catalysts was further investigated by 100 cycles of CV scan at a faster rate (10 mV s<sup>-1</sup>). An increase of pseudocapacitive currents was observed from hydro-LCG, while the catalytic current remained about the same (Figure The increase of pseudocapactance was previously 5(c)). reported on LiCoPO<sub>4</sub> as OER catalyst, which was attributed to structural and chemical transformation of catalyst based on a thorough investigation using HR-TEM.9 Survey of hydro-LCG before and after CV cycles with SEM did not reveal much morphology change at µm-scale (Figure 6), although compositional change was very significant as observed by EDX analysis. Pristine hydro-LCG has a Ge:Co atomic ratio of 1:1, which did not change after being soaked in 0.1 M NaOH for 4 hr (about same time as it takes to complete 100 CV cycles at 10 mV·s<sup>-1</sup>). However, this ratio decreased to  $0.14\pm0.02$  (average of eight independent spectra analyses) after 100 CV cycles, indicating an essential loss of Ge from the catalyst since cobalt is known not soluble at pH 13.40 Furthermore, a loss of ~50% of Li was also detected from hydro-LCG by ICP analysis after 100 of cycles. Along with the compositional changes, HR-TEM images revealed profound differences from catalyst surface before and after CV cycles (Figure 6). While pristine hydro-LCG is highly crystalline, amorphization can be seen clearly from catalyst surface after even the first cycle of CV scan, and became much more severe after 100 cycles.

XPS analysis was conducted on fresh and used hydro-LCG electrodes to further probe the possible changes to the catalyst surface during OER. After being used for OER, the colour of the catalyst film changed from blue to dark brown (Figure 7). Co 2p spectrum from fresh hydro-LCG has a very characteristic  $Co^{2+}$  signal with two main peaks at 797.1 and 781.1 eV for the  $2p_{1/2}$  and  $2p_{3/2}$  regions and the corresponding satellite peaks at 802.7 and 786.8 eV, respectively. After use the hydro-LCG XPS spectra resembled closely to  $Co_3O_4$  standard in the  $2p_{3/2}$  and  $2p_{1/2}$  regions with the positions of the main peaks shifting to lower energy and a decrease of relative intensity of satellite peaks to the main peaks (Figure 7). These changes typically indicate a transition from high spin  $Co^{2+}$  to  $Co^{3+}, 3^{4-38}$  which also corresponds well with the previously reported colour change of other  $Co^{2+}$  containing OER that oxidize to  $Co^{3+}, 2^{2,39}$ 



**Figure 7.** XPS spectra of dip coated hydro-LCG (i) before and (ii) after applying 1.7 V for 2 h as well as (iii)  $Co_3O_4$  as a standard. Photos on right hand side show colour of the electrode before (top) and after (down) being used for OER.

Although collective evidences from CV, HR-TEM, XPS and compositional analyses suggest that structure and composition of hydro-LCG evolved during OER process, completely understanding the active site structure and reaction mechanism is not trivial and largely beyond the scope of this study. The initial oxidation of Co from 2+ to 3+, as observed from LSV and forward scan of 1<sup>st</sup> CV cycle, might have triggered the disruption of catalyst surface structure and the loss of Li and Ge. As such amorphization progresses deeper into bulk catalyst, it apparently did not create more active sites at outer layer of the catalyst because there was no increase of catalytic current, but resulted in larger area of internal grain boundaries, which corresponds to the rise of pseudocapactance. In reference to a previous report of amorphization of LiCoO<sub>2</sub> and LiCoPO<sub>4</sub> for OER in alkaline electrolytes<sup>9</sup>, we believe the active sites of the evolved hydro-LCG resemble more to those from LiCoPO<sub>4</sub>, because of i) similar Tafel slopes, ii) significant loss of Ge or P during CV scans, iii) retention of about half of Li from hydro-LCG after 100 CV cycles, and most importantly, iv) the absence of a second pair of redox peaks at  $\sim$ 1.41 V vs. RHE observed as a distinct feature of amorphized LiCoO<sub>2</sub>.

#### Conclusions

We have shown that  $Li_2CoGeO_4$  can be synthesized hydrothermally at a temperature much lower than previously

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reported solid state methods. The hydrothermally synthesized  $Li_2CoGeO_4$  was found to be isostructural with  $Li_2ZnGeO_4$ , which is different from the previously reported two structure models. Electrochemical characterization confirmed  $Li_2CoGeO_4$  was catalytically active towards OER in alkaline electrolyte with performance better than  $Co_3O_4$ . Further characterization of the catalyst with CV, HR-TEM, XPS and elemental analyses revealed the oxidation of cobalt from 2+ to 3+ during OER process, along with significant surface amorphization and loss of Li and Ge from the catalyst.

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Electronic Supplementary Information (ESI) available: details of structure refinements using different space group models, full range XRD spectra from DFT calculations, energy calculated by DFT and galvanostatic analysis of hydro-LCG and  $Co_3O_4$  at 50  $\mu$ A/cm<sup>2</sup><sub>catalyst</sub>. See DOI: 10.1039/b00000x/

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Table of content entry

We report hydrothermal synthesis and structural refinement of  $Li_2CoGeO_4$ , as well as its use as catalyst for oxygen evolution reaction.

