

Antiferromagnetic inverse spinel oxide LiCoVO_4 with spin-polarized channels for water oxidation

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Abstract

Exploring highly efficient catalysts for the oxygen evolution reaction (OER) is essential for water electrolysis. Cost-effective transition-metal oxides with reasonable activity are raising attention. Recently, the OER reactants' and products' differing spin configurations have been thought to cause slow reaction kinetics. Catalysts with magnetically polarized channels could selectively remove electrons with opposite magnetic moment and conserve overall spin during OER, enhancing triplet state oxygen molecule evolution. Here, antiferromagnetic inverse spinel oxide LiCoVO_4 is found to contain $d^7 \text{Co}^{2+}$ ions that can be stabilized under active octahedral sites, possessing high spin states $S=3/2$ ($t_{2g}^5 e_g^2$). With high spin configuration, each Co^{2+} ion has an ideal magnetic moment of $3\mu_B$, allowing the edge-shared Co^{2+} octahedra in spinel to be magnetically polarized. Density functional theory (DFT) simulation results show that the layered antiferromagnetic LiCoVO_4 studied contains magnetically polarized channels. The average magnetic moment (μ_{ave}) per transition-metal atom in the spin conduction channel is around $2.66\mu_B$. Such channels are able to enhance the selective removal of spin-oriented electrons from the reactants during the OER, which facilitates the accumulation of appropriate magnetic moments for triplet oxygen molecule evolution. In addition, the LiCoVO_4 reported has been identified as an oxide catalyst with excellent OER activity.

Introduction

Across centuries of industrialization and urbanisation, fossil fuels have played an important role in energy supply. However, the consumption of fossil fuels causes harmful environmental impacts. Thus, the development of clean and renewable energy sources has become necessary. The intermittent nature of such energy sources necessitates the development of suitable methods for energy conversion and storage. Electrochemical water splitting is one such storage and conversion technique that is becoming more prominent.^[1] The electrochemical water splitting process involves two half-cell reactions: the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER). Compared to the HER, the OER has slower reaction kinetics as it involves a four-step electron transfer and involves multiple reaction intermediates.^[2] In order to lower the OER reaction barrier, good catalysts are essential. Currently, the most active catalysts for OER are RuO₂ and IrO₂.^[2a] However, Ru and Ir are rare earth elements with very high commercial prices, which hinders the practical application of these catalysts. Thus, there is a need to investigate promising catalysts for the OER, which are composed of earth-abundant elements and are also cost-effective.

Transition metal oxides have attracted attention in recent years, as they are cost-effective, earth-abundant, and have competitive OER catalytic activity. Earth-abundant cobalt oxides like spinel Co₃O₄, layered LiCoO₂, and perovskite Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-σ} (BSCF) and CaCu₃Fe₄O₁₂ (CCFO) are some of the most efficient transition metal based OER catalysts.^[3] In order to design effective Co-based catalysts, the research community has proposed several descriptors. One such

descriptor was proposed by Shao-Horn and co-workers, who reported the e_g theory which links the M-O binding energy to the active transition metal ion's e_g value to guide the design of perovskite OER catalysts.^[3a] According to this design guideline, BSCF with an average e_g filling of 1.1 for B-site cations was discovered to exhibit the highest OER activity.^[3a] As for spinel oxide OER catalysts, cations in octahedral sites are reported to be the OER active sites.^[4] Thus, e_g theory is also a valid design guideline for spinel oxide catalysts. However, e_g theory has some limitations. It is very difficult to accurately estimate the e_g value, and it is challenging to identify the active sites for a complex oxide system. Recently, the different spin configuration between OER reactants and product has attracted attention. According to previous studies, the reaction is slow if the reactants and products have different spin polarization.^[5] With that, a comprehensive theoretical study of spin transportation and conservation in OER catalysis was conducted by Gracia et al.^[6] He proposed that the contribution of active sites' e_g electron to their magnetic moment, μ_B^{eg} , as a OER descriptor for perovskites.^[6] Besides having the optimal μ_B^{eg} value, the most active perovskite OER catalysts exhibit spin-selective conduction channels at electronic ground states.^[5b, 6] As they reported, most of the octahedral cobalt ions (CoO_6) that exist in perovskite and spinel structures have a valence state of +3. Co^{3+} ions under an octahedral crystal field are low spin ($t_{2g}^6 e_g^0$) and the fully paired d electrons lead to a net magnetic moment of zero.^[2b, 7] However, if d^7 Co^{2+} ions can be stabilized under active octahedral sites, they are expected to possess high spin state $S=3/2$ ($t_{2g}^5 e_g^2$).^[8] With high spin configuration each Co^{2+} ion have an ideal magnetic moment of $3\mu_B$, the edge-shared Co^{2+} octahedra in spinel could be magnetically polarized.^[9]

In this report, we investigated LiCoVO_4 , which has an inverse spinel structure with the unique property of Co^{2+} stabilized in octahedral sites ($\text{Co}^{2+}_{\text{Oh}}$).^[10] In comparison, normal spinel ZnCo_2O_4 with Co^{3+} in octahedral sites ($\text{Co}^{3+}_{\text{Oh}}$) was also studied.

LiCoVO_4 was found to exhibit a high OER activity compared to ZnCo_2O_4 . It appears that the high spin Co^{2+} ($S=3/2$) in bulk octahedron promotes OER activity through a spin-polarized channels for better electron transfer. Density functional theory (DFT) calculation shows that the layered antiferromagnetic LiCoVO_4 inverse spinel oxide contains magnetically polarized channels. The average magnetic moment (μ_{ave}) per transition-metal atom in the spin conduction channel is around $2.66\mu_{\text{B}}$. Such channels are able to enhance the selective removal of spin-oriented electrons from the reactants during OER, which facilitates the accumulation of appropriate magnetic moments for triplet oxygen molecule evolution.^[5b, 6] In addition, the LiCoVO_4 reported has been identified as a new oxide catalyst with the excellent OER activity.

Material characterization

Inverse spinel oxide LiCoVO_4 with $\text{Co}^{2+}_{\text{Oh}}$ was synthesised using sol-gel methods.^[11] The ZnCo_2O_4 spinel oxide with $\text{Co}^{3+}_{\text{Oh}}$ was synthesised according to the previous report.^[12] The X-ray diffraction patterns of LiCoVO_4 and ZnCo_2O_4 are shown in Figure 1a. LiCoVO_4 and ZnCo_2O_4 exhibit the cubic-spinel structure with $\text{Fd}\bar{3}\text{m}$ space group. The XRD patterns exhibit a weak (111) peak at 18.59° and a relatively strong (022) peak at 30.53° , indirectly indicating that the LiCoVO_4 oxide has inverse spinel structure.^[10c, 13] Previous reports have shown that vanadium ions occupying tetrahedral sites would lead to an increase in (022) peak intensity at the expense of (111) peak intensity, explaining these results.^[13-14] Scanning electron microscope (SEM) images of the synthesized LiCoVO_4 and ZnCo_2O_4 are shown in Figure S1.

The X-ray absorption near edge structure (XANES) technique was used to reveal the valence states of cobalt ions and the vanadium ions. The position of the XANES absorption edge provides information of the metal cation's valence state.^[15] Figure 1b confirms Co^{2+} ions are presented in LiCoVO_4 and Co^{3+} ions are presented in ZnCo_2O_4 . The valence state of vanadium ion is 5+ (Figure 1d), and it is double confirmed by XPS. Figure 1c shows the V2p spectra, the energy difference between $\text{V}2p_{3/2}$ and $\text{V}2p_{1/2}$ is 7.33eV which indicates vanadium ions are 5+.^[16] The coordination environment and structural position of V^{5+} , Co^{2+} ions were revealed by extended X-ray absorption fine structure (EXAFS). In Figure S2a, the Co-O bond length is 1.61 Å (peak 1) which is longer than the Co-O bond length in past reports (approximate 1.5 Å^[15a, 17]). This is due to cobalt ions having a low valence state of 2+, which leads to a longer Co-O bond length. Peak 2 located at 2.75 Å represents Co- Co_{Oh} , indicating that Co^{2+} ions mainly occupy octahedral sites.^[16b, 18] As shown in Figure S2b, Peak 1 located at 1.36 Å, which is associated with the scattering path from V^{5+} ion to its nearest neighbour oxygen ion, represents the V-O bond length. Peak 2 located at around 3.03 Å represents the scattering path from the metal ions to their nearest metal ions in tetrahedral geometric sites.^[16b, 18] Fourier-transform infrared (FTIR) measurement was also conducted to double confirmed the vanadium ions' coordination environment. In Figure S3, a vibration peak at 700-850 cm^{-1} was observed, which is mainly contributed by VO_4 tetrahedron stretching vibration.^[14, 16b] This confirmed vanadium ions located in tetrahedral geometric sites.

OER performance evaluation

The OER performance was evaluated using cyclic voltammetry (CV) technique under 1M KOH alkaline conditions with a three-electrode setup. CV potential range was

from 0.9 to 1.6V (vs RHE) with a scan rate of 10mV/s. The OER current densities are normalised by BET surface area to present the intrinsic catalytic activity.^[19] And the iR correction was applied to calibrate the working potential. In both ZnCo₂O₄ and LiCoVO₄ the cobalt ions are the active sites as other cation ions are OER inert d⁰ metal cations.^[15a] LiCoVO₄ shows much better performance compared to ZnCo₂O₄ (Figure 2a). This indicates that Co²⁺ octahedron is more active compare to Co³⁺ octahedron. The redox peak at 1.1V (Figure 2a) is standard Co²⁺/Co³⁺ redox peak,^[15a] which also indicate the existence of Co²⁺ ions in LiCoVO₄. The charges associated with Co²⁺/Co³⁺ oxidation and reduction peaks are shown in Figure 2a. Negligible charge difference of 0.37E-5 C indicates that Co²⁺/Co³⁺ redox pair is highly reversible. Co ions' valence state in bulk pristine LiCoVO₄ and cycle LiCoVO₄ is evaluated by XAS. Figure 2e shows the Co ions remain 2+ valence state after CV cycling. Co 2p_{3/2} XPS results of pristine and cycled LiCoVO₄ are shown in Figure 2c and 2d. The satellite peak at 786eV is a strong evidence for Co²⁺ ions.^[20] The Co²⁺/(Co²⁺ + Co³⁺) peak area ratios (Figure 2d) of pristine (57.6%) and cycled LiCoVO₄ (56.3%) are almost the same. This again proves the Co³⁺ ions are fully reduced to Co²⁺ ions during the cathodic CV sweep. It is worth to know that the small portion of Co³⁺ on the LiCoVO₄ surface will not affect the spin channels inside the bulk oxide. The spin channels are composed by edge-shared Co²⁺ octahedra which exist in the bulk crystal. TEM images (Figure 2f and Figure 2g) of pristine and cycled LiCoVO₄ indicates that there is no remarkable surface reconstruction during OER. The Tafel plot (Figure 2b) shows that LiCoVO₄ has better OER activity than IrO₂ and its OER activity is competitive to the most active oxide-based catalyst Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} (BSCF).

Electronic structure and magnetic properties studies of ZnCo₂O₄ and LiCoVO₄

In order to understand the fundamentals of the tested OER active spinel oxides, the magnetic property and electronic structure of the oxides were investigated. According to Figure 3c and 3d, LiCoVO_4 has very small magnetic susceptibility and negative interception of $1/\chi$, thus LiCoVO_4 is antiferromagnetic. DFT simulation with antiferromagnetic ground states was carried out to investigate the electronic structure of LiCoVO_4 . The computed partial density of states (pDOS) of LiCoVO_4 and ZnCo_2O_4 are shown in Figure 3. The ZnCo_2O_4 shows a symmetric pDOS (Figure 3a) with a band gap of $\sim 1.7\text{eV}$, which is consistent with previous report.^[21] In ZnCo_2O_4 the Co^{3+} ions locate under a octahedral field with all paired valence electrons lead to a net zero spin value. The LiCoVO_4 also shows a symmetric pDOS (Figure 3b) with a smaller band gap 1.36eV . Thus, the electrons in LiCoVO_4 are easier to be excited into the conduction band and transfer away. And significant overlapping between O-2p orbital and Co-3d orbitals of LiCoVO_4 at near Fermi region could be observed. However, ZnCo_2O_4 does not exhibit such strong Co-3d and O-2p orbital overlapping. This indicates the LiCoVO_4 has stronger Co-O bond covalency that leads to better OER performance, which also consist with previous reports.^[21a, 22] The magnetic properties of ZnCo_2O_4 and LiCoVO_4 were investigated by vibrating-sample magnetometer (VSM) method. As shown in Figure 3c, linear hysteresis loops of ZnCo_2O_4 and LiCoVO_4 with very small slopes are observed. The magnetic susceptibility of ZnCo_2O_4 and LiCoVO_4 are $6.6\text{E-}6$ and $6.1\text{E-}5$ emu/gOe, respectively. In Figure 3d and Figure S6, the reciprocal of magnetic susceptibility is plotted against temperature and linear fitting was conducted. The interception of $1/\chi$ of both ZnCo_2O_4 (-146.7K) and LiCoVO_4 (-14.9K) are found to be negative. The small magnetic susceptibility and negative interception of $1/\chi$ indicate that ZnCo_2O_4 and LiCoVO_4 are antiferromagnetic.^[23] This result is consist with DFT simulation

result. According to DFT simulation result, LiCoVO_4 exhibits layered antiferromagnetic structure as shown in Figure S5. The magnetisms from spin-up Co^{2+} layer and Co^{2+} spin-down layer are cancelled each other, resulting in zero net magnetism. The enhancement of OER catalytic activity by magnetic field was recently reported by José Ramón Galán-Mascarós et al.^[24] The founding shown that the magnetic enhancement of catalysts' OER activity have certain correlation to the catalysts' bulk magnetization. Under moderate magnetic field, materials with higher bulk magnetization exhibit larger enhancement of their OER activities.^[24] Therefore, we investigated the effect of an external magnetic field on LiCoVO_4 and ZnCo_2O_4 by applying a 250mT magnetic field during chronoamperometry (CA) measurement. The results (Figure S7 and S8) indicate that the external magnetic field does not enhance their OER activity. Because both LiCoVO_4 and ZnCo_2O_4 are antiferromagnetic materials with very low magnetic susceptibility, an external magnetic field is not expected to enhance their OER activity, which is consistent with the previous report.^[24] The external magnetic field has no effect on LiCoVO_4 OER performance also indicates that the Co^{2+} ions with positive and negative magnetic moments alternating with layer arrangement is stable in bulk oxide at room temperature.

Spin polarized channel of LiCoVO_4 facilitating OER performance

The crystal structure and planar view along the [001] direction of the spinel is shown in Figure 4a. The spin distribution of ZnCo_2O_4 is presented in Figure 4c. This material contains edge-shared Co^{3+} ions with symmetric spin-up and spin-down electrons (paired electrons), that result in zero magnetization for Co^{3+} ions. Thus, the edge-shared octahedron channels in ZnCo_2O_4 have zero net magnetism. In LiCoVO_4 , Co^{2+} and Li^+ ions are located in edge-shared octahedral sites. The OER active Co^{2+}

ions here possess high spin configuration ($t_{2g}^5 e_g^2$). Each Co^{2+} ion has a magnetic moment of $\pm 2.66\mu_B$ (Figure 4b, 4e and Figure S5) with positive and negative moments alternating with layer. The oxygen ions bound to them also have a small magnetic moment ($\pm 0.016\mu_B$), which is caused by spin donation from the Co^{2+} ion through $\text{Co}_{3d}-\text{O}_{2p}$ orbital overlapping.^[5b] Compared to ZnCo_2O_4 , these edge-shared octahedron channels in LiCoVO_4 are magnetically polarized. According to previous studies, electrons with opposite spin direction have weaker scattering effects when such electrons transfer through the magnetic lattice.^[5b, 25] Thus, the magnetic polarised channels in LiCoVO_4 (Figure 4e, S5) would act as spin-selective conduction channels with smaller electron transfer barrier for the electrons with the opposite spin. In the oxygen evolution reaction, the reactants have singlet configuration but the final product is a triplet molecule. The differing spin configuration between reactants and products leads to a slower reaction as the spin is not conserved.^[5b] Therefore, extra energy or stimulus for spin coupling is needed to trigger this reaction.^[5] In the LiCoVO_4 system, the Co-O bonds along the magnetically polarized channels have certain spin character which is caused by spill-over of Co^{2+} magnetic polarization through $\text{Co}_{3d}-\text{O}_{2p}$ overlapping. According to Gracia's recently proposed mechanism,^[5b, 6] under an applied working potential, the active sites on the magnetically polarized channels could extract spin-oriented electrons from reactants and transfer them through the aforementioned channels. This process would break the electron pairs on the adsorbates and promote accumulation of appropriate magnetic moment on the active sites. This facilitates the formation of triplet oxygen molecules (Figure 5b). Thus, LiCoVO_4 exhibits excellent OER performance.

Summary

In summary, as-synthesized LiCoVO_4 inverse spinel oxide successfully stabilized Co^{2+} ions in octahedral sites. Compared to ZnCo_2O_4 , $\mu_{\text{B}}^{\text{eg}}$ value of OER active sites in LiCoVO_4 is optimized. At the same time, LiCoVO_4 shows stronger Co-O bond covalency than ZnCo_2O_4 , which further promotes its OER performance. Besides that, layered antiferromagnetic LiCoVO_4 also contains magnetically polarized channels. Under applied potential, active sites in those channels may facilitate the extraction of certain spin-oriented electrons from the singlet reactants. This leads to accumulation of magnetic moments at the intermediate/catalyst interface, boosting triplet oxygen evolution. The LiCoVO_4 oxide appears to allow for spin conservation throughout the reaction, which also leads to good OER performance.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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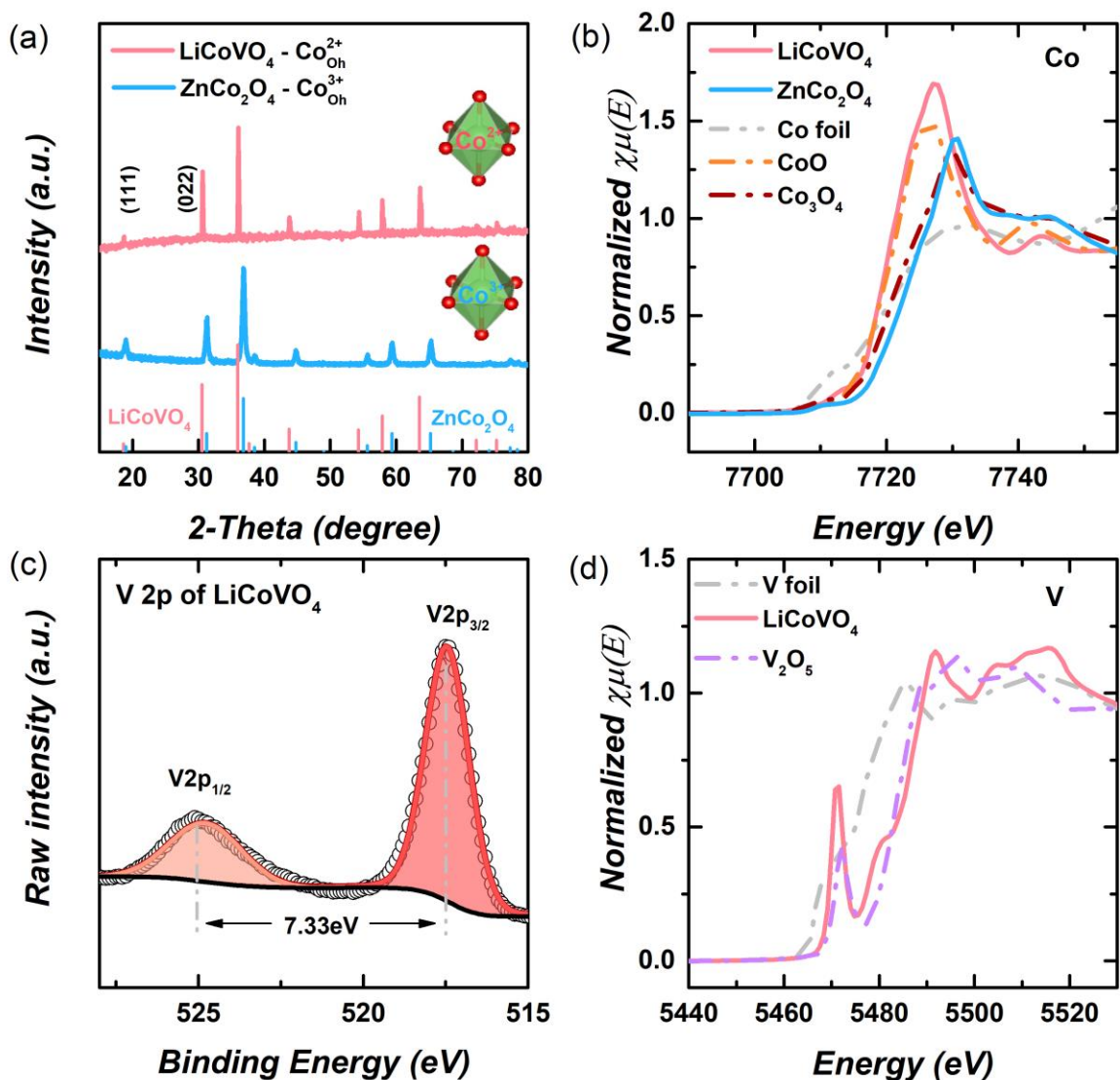


Figure 1. (a) XRD patterns of LiCoVO_4 and ZnCo_2O_4 . (b) Normalized Co K-edge XANES spectra of LiCoVO_4 and ZnCo_2O_4 . (c) V 2p XPS spectra of LiCoVO_4 . (d) Normalized V K-edge XANES spectra of LiCoVO_4 .

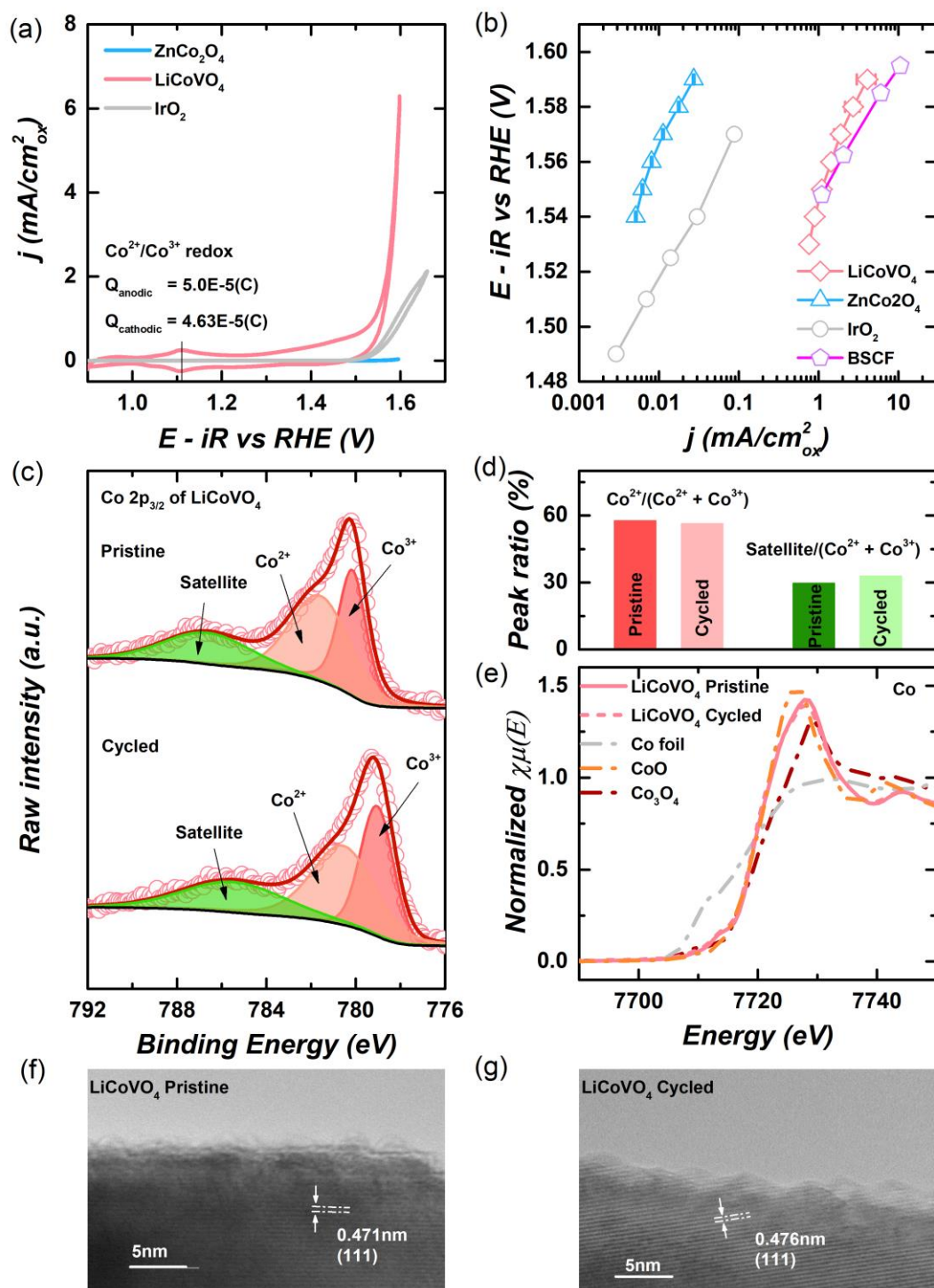


Figure 2. (a) Representative CV curves (2nd cycle) of LiCoVO₄, ZnCo₂O₄ and IrO₂. (b) The Tafel plot comparison, benchmark IrO₂ and BSCF tafel extract from ref 3. (c) Co 2p_{3/2} XPS spectra of pristine and cycled LiCoVO₄. (d) XPS peak area ratios. (e) Normalized Co K-edge XANES spectra of pristine LiCoVO₄ and cycled LiCoVO₄. (f) TEM image of pristine LiCoVO₄. (g) TEM image of cycled LiCoVO₄. Cycled LiCoVO₄ indicates sample after 100 cycles CV.

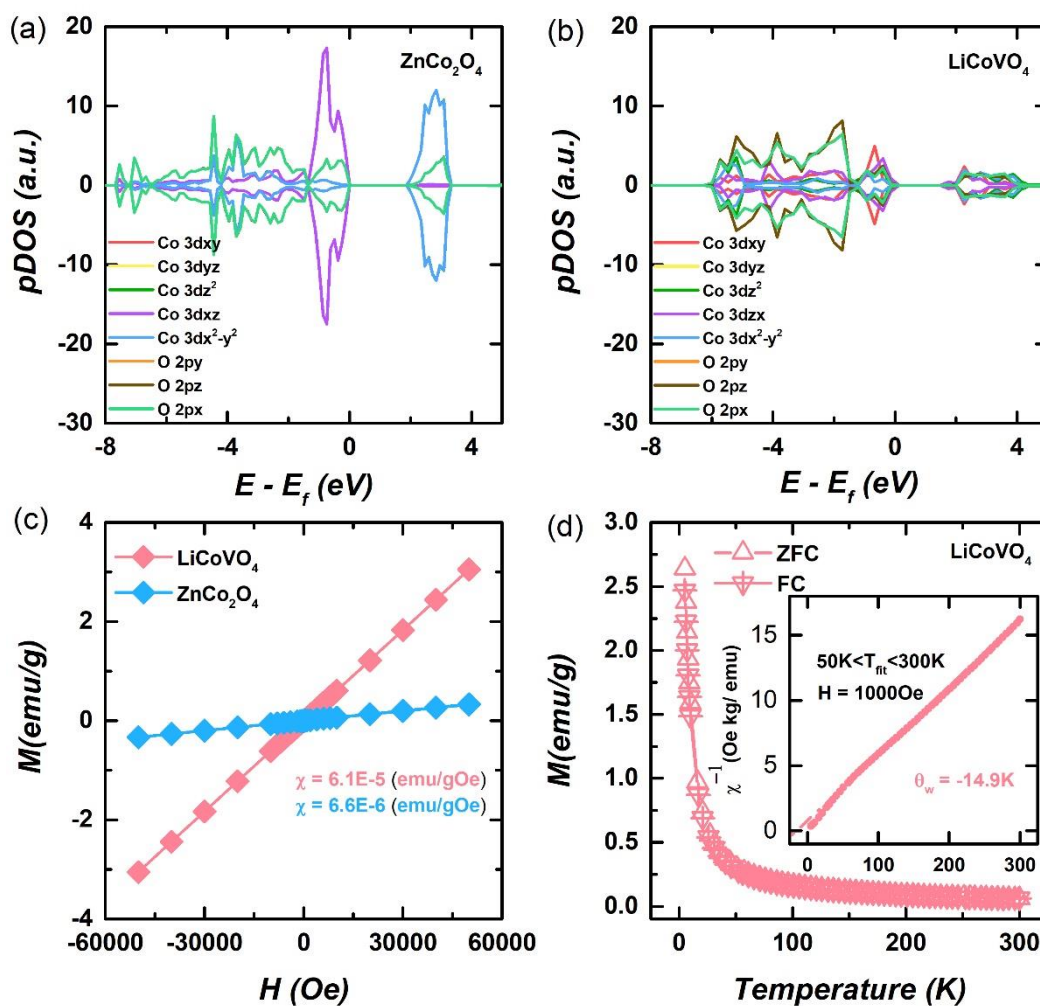


Figure 3. (a) pDOS of ZnCo₂O₄. (b) pDOS of LiCoVO₄. (c) Hysteresis curves of LiCoVO₄ and ZnCo₂O₄. (d) Field-cooled and zero-field-cooled susceptibility plotted versus temperature for LiCoVO₄, insert is the Curie-Weiss plot of LiCoVO₄.

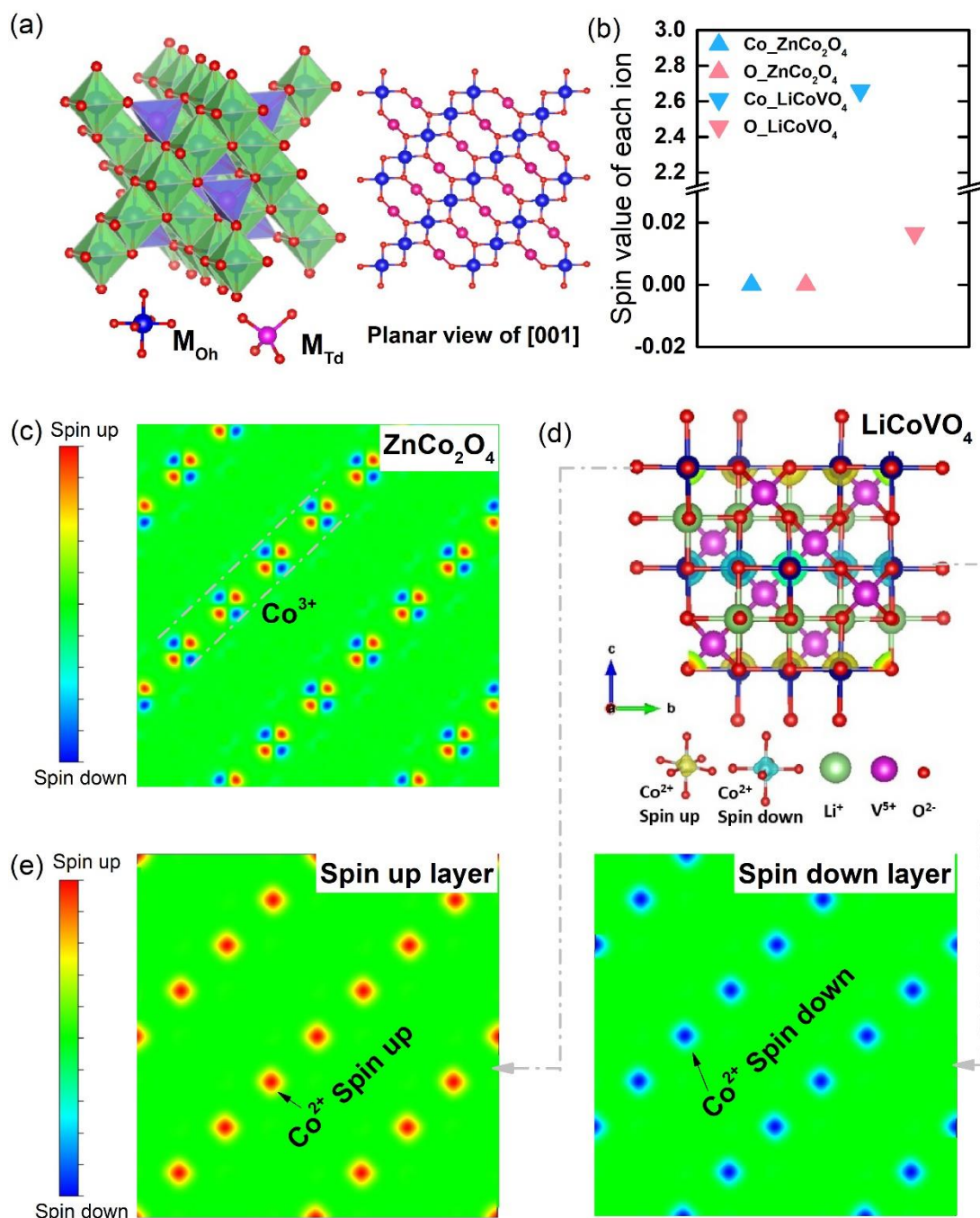


Figure 4. (a) Crystal structure of typical cubic spinel oxide and planar view along [001] direction. (b) The spin value magnitudes of Co and O ions of $LiCoVO_4$ and $ZnCo_2O_4$ along the spin channels. (c) Spin distribution map of $ZnCo_2O_4$ (111) plane, red indicates spin up, blue indicates spin down. (d) Crystal structure of $LiCoVO_4$ with spin isosurface, ions with yellow color isosurface indicates net up spin, ions with blue color isosurface indicates net down spin, ions without isosurface indicates net spin is zero. (e) Spin distribution map of spin up and spin down layers in $LiCoVO_4$ along [001] direction.

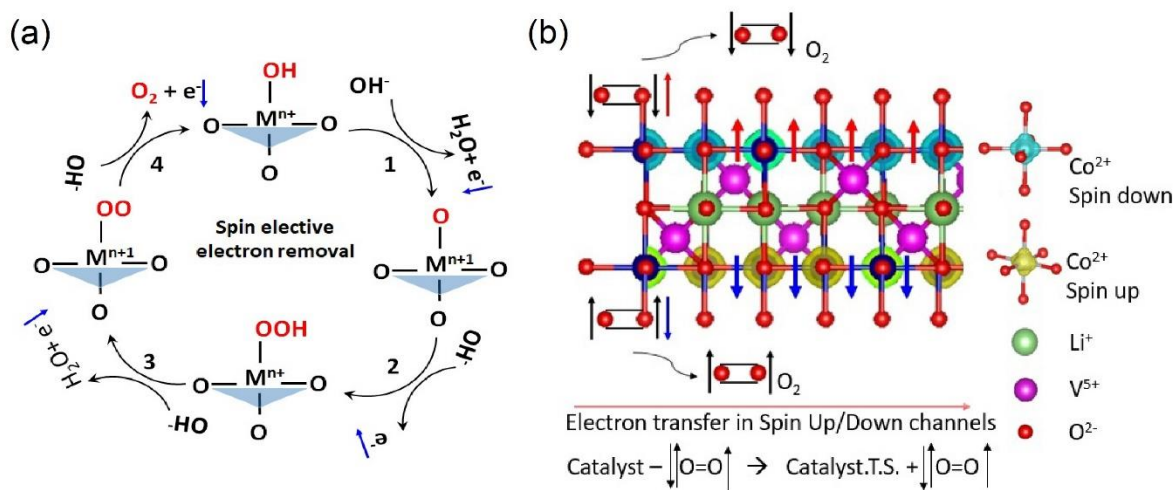


Figure 5. (a) The spin selective OER reaction mechanism. (b) Spin selective electron transfer in layered antiferromagnetic LiCoVO_4 .

Antiferromagnetic inverse spinel oxide LiCoVO_4 is found to contain spin-polarized channels. Such channels could enhance selective removal of spin-oriented electrons from the reactants during the OER, which facilitates the accumulation of appropriate magnetic moments for triplet oxygen molecule evolution and conserves the overall spin during the OER.

Keyword electrocatalysis; water oxidation; antiferromagnetic; inverse spinel oxide; spin polarized channels

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