Electrochemical Tuning of Electronic Structures for Highly Active Electro catalysts

Investigators
Prof. Yi Cui, Material Sciences and Engineering; Prof. Harold Hwang, Applied Physics; Wei Chen, Guangxu Chen, Zhiyi Lu, post-doctoral researchers, Material Sciences and Engineering; Haotian Wang, Yayuan Liu, graduate researchers, Material Sciences and Engineering, Stanford University.

Abstract
Electrochemical reactions, such as hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and oxygen reduction reaction (ORR), play critical roles in a number of clean energy processes. Exploring highly efficient electrocatalysts is of great importance to maximize the efficiencies of these processes. In this final report, we summarize the significant progresses we achieved in the past three years on exploring efficient catalysts by the strategy of electrochemical tuning. The catalysts shown here include transition metal oxides, lithium transition metal phosphate, transition metal sulfides and noble metal/transition metal oxides mixture. In the first case, we observe that, after several times of inserting and extracting lithium into and out of the transition metal oxides, the catalysts become very porous with ultra-small interconnected nanoparticles, which provide a large amount of active sites and result in significantly enhanced OER and HER performance in base electrolyte. In the second case, by continuously extracting lithium out from lithium transition metal phosphates, the catalysts become more efficient for water oxidation. Thirdly, we have developed an in situ electrochemical oxidation tuning approach to develop a series of binary, ternary, and quaternary transition metal (e.g., Co, Ni, Fe) oxides from their corresponding sulfides as highly active catalysts for water oxidation. Last but not least, a method for using battery electrode materials to directly and continuously control the lattice strain of platinum catalyst is developed, and correspondingly the ORR activity of the catalyst can be precisely tuned.

Introduction
The ever increasing global reliance on non-renewable energy resources and the rapid depletion of fossil fuels are vital challenging issues which promotes the development of renewable energies as well as the devices for efficient energy storage and conversion (e.g. water splitting to generate hydrogen, metal-air batteries and fuel cells)[1-3]. These energy storage and conversion processes contain a variety of electrochemical reactions, where the representative and important reactions are HER, OER and ORR. A very important step to maximize the energy efficiency of these three reactions is to explore highly efficient electrocatalysts which are not only highly active and stable but also low cost. Although precious metal-based materials, such as Pt, Ir and Ru, are currently the most efficient electrocatalysts for these important reactions, their scarcity and high cost make them difficult for large scale applications. Thereby, alternative materials based on low-cost elements have been widely investigated, but most of the non-precious metal catalysts still underperform their
precious metal counterparts. Thus, it is intriguing to develop strategies for improving the electrocatalytic activity and stability of existing materials.

In recent decades, the most common approach to achieve a high efficient catalyst is to fabricate new materials with desirable chemical compositions and morphologies. To be general and tunable, we have developed a completely different strategy by electrochemically tuning the existing catalysts over a wide dynamic range of electrochemical potential to explore superior catalysts. In this tuning strategy, we use electrochemical insertion or extraction of Li ions into or out of catalyst materials to control electrochemical potential, crystal structure, surface structure and electronic structure over a wide range (up to a few volts), which are specifically for HER, OER and ORR. Our previous studies have demonstrated that intercalating lithium into two-dimensional MoS$_2$ and extracting lithium out of LiCoO$_2$ can affect the electronic structure of the catalysts, resulting in much enhanced HER and OER performances[4, 5]. These successful demonstrations motivate us to keep applying this methodology for other materials and investigating the possible mechanisms.

Background

The target reactions (HER, OER and ORR) we investigated in this project are essential parts in current energy conversion processes and electrocatalytic industrial production. For instance, water splitting, which is believed one of the most promising ways to store solar energy, contains both HER and OER. Moreover, HER is also playing a very important role in chlor-alkali industry. In metal-air batteries or fuel cells, ORR happens on anodes to generate hydroxide anions.

HER is a process to produce H$_2$ from water, a cathodic half reaction of water splitting and involving two electron transfers. Due to the appropriate binding energy to the hydrogen atom (not too strong or not too weak), Pt-based catalysts are the most effective electrocatalysts to date with negligible overpotential. Based on this principle, more economical electrocatalysts based on non-precious metals are explored recently, including transition metal chalcogenides, carbides, phosphide and so on, even though they are still less effective or stable than Pt-based electrocatalysts[6-9]. Therefore, the HER performance of these low-cost alternatives need to be further improved.

OER is another half reaction of water splitting, which generates O$_2$ through electrochemical oxidation of water, and it is also a key reaction for rechargeable metal-air batteries. Since multistep proton-coupled electron transfer processes are involved in OER, the kinetics are usually sluggish[10]. An effective electrocatalyst is needed to accelerate this reaction, and thus enhance the energy conversion efficiency. Currently, the most active OER catalysts are RuO$_2$ or IrO$_2$ in acidic or alkaline solutions, but the required operating potentials of these catalysts are still far from the thermodynamic potentials (~200 mV overpotential)[11, 12]. In addition, the cost and supply issues also restrict their commercial realization. Recently, there are several theoretical simulation and experimental evidence showing that the first-row transition metal compounds can exhibit extraordinary OER activities by optimizing the electronic structure of transition metal ions, such as oxidation state, eg filling and O p-band center[13-15]. Following these principles, many electrocatalysts have been
identified, such as transition metal oxides, perovskites as well as other compounds [16, 17]. However, the performances are still unsatisfied. Therefore, low-cost electrocatalysts with desirable OER activity are still needed.

ORR, as a reverse reaction of OER, is the cathode reaction for a range of energy applications, including fuel cells and metal-air batteries. The kinetics of ORR are very sluggish because it is hard to break the strong O=O bond, which requires four coupled electron and proton transfers. Therefore, various materials have been investigated as catalysts to enhance ORR activity and platinum-based materials (Pt and its alloys) are the most widely used catalysts for ORR with low overpotential and good stability. However, even for the expensive Pt-based catalysts, the onset potential for ORR (~0.95 V) is still far from the equilibrium potential (1.23 V vs. RHE), which induces significant energy loss for operating this reaction. Low-cost alternatives, such as metal-N complexes on carbon support [18-20], metal chalcogenides, spinel oxides [21, 22], and doped carbonaceous materials [23, 24] have been explored with promising advances. Despite this progress, it is still challenging to develop low-cost ORR catalysts with high activities comparable to or exceeding Pt-based materials and similar or higher stability than Pt-based materials.

The aforementioned three electrochemical reactions are of great importance for maximizing the efficiency of current energy conversion and storage processes. Simple calculations may make it easier to understand how much energy we can save by enhancing the catalytic activity of the catalysts for those three important reactions. Here we use the zinc-air battery which involves OER and ORR catalysis as an example. The benchmarks of OER and ORR in alkaline solution are IrO$_2$ and Pt respectively. The onset potential of IrO$_2$ and Pt are located at around 200 mV and 300 mV away from the thermodynamic potential (1.23 V), so that the full cycle of oxygen evolution and reduction will lose 40% of the available energy. However, the current non-precious catalysts mentioned above for OER and ORR are usually around 350 mV and 450 mV away from the equilibrium potential, losing even more energy of ~65%. Therefore, if the overpotentials for both OER and ORR can be reduced to ~100 and ~200 mV, respectively, only 20% of energy will be lost for this kind of rechargeable battery. Therefore, developing a useful and powerful methodology for better non-precious electrochemical catalysts screening is meaningful to renewable energy usage and storage.
Results

*Lithium induced conversion reaction on transition metals oxides for overall water splitting*

**Figure 1** Schematic of TMO morphology evolution under galvanostatic cycles and the catalytic performance of bifunctional catalyst over overall water splitting. (a–e) TMO particles gradually change from single crystalline to ultra-small interconnected crystalline NPs. Long-term battery cycling may result in the break-up of the particle. (f) The galvanostatic cycling profile of CoO/CNF galvanostatic cycling. (g) The HER activity of 2-cycle NiFeO$_x$/CFP is significantly improved from its pristine counterpart and close to the Pt/C benchmark. (h) Two-cycle NiFeO$_x$/CFP as HER and OER bifunctional catalyst in 1M KOH for overall water splitting. Ir/C and Pt/C as OER and HER benchmarks are tested side by side. With the mass loading increased from 1.6 to 3 mg cm$^{-2}$ (the dash line), the water-splitting activity of 2-cycle NiFeO$_x$/CFP outperforms the benchmark combination. (i) Long-term stability of 2-cycle NiFeO$_x$/CFP bifunctional catalyst. The voltage to achieve 10mA cm$^{-2}$ electrolysis current shows an activation process, followed by a stable 1.55V for 100h continuous operation. As a sharp contrast, Ir and Pt combination shows an efficient starting voltage but followed by a fast decay. By increasing the mass loading to 3 mg cm$^{-2}$, 2-
cycle NiFeOₓ/CFP further lowers the voltage to 1.51V to achieve 10mA cm⁻² current density for over 200 h without decay.

We firstly demonstrate the effectiveness of lithium tuning method on the transition metal oxides. It is found that both the OER and HER activities of the transition metal oxides can be significantly enhanced when transition metal oxide (iron, cobalt, nickel oxides and their mixed oxides) nanoparticles (~20 nm) are electrochemically transformed into ultra-small diameter (2–5 nm) nanoparticles through lithium-induced conversion reactions (Figure 1). Different from most traditional chemical syntheses, this method maintains excellent electrical interconnection among nanoparticles and results in large surface areas and many catalytically active sites. We demonstrate that lithium-induced ultra-small NiFeOₓ nanoparticles are active bifunctional catalysts exhibiting high activity and stability for overall water splitting in base. We achieve 10 mA cm⁻² water-splitting current at only 1.51V for over 200 h without degradation in a two-electrode configuration and 1M KOH, better than the combination of iridium and platinum as benchmark catalysts[25].

Lithium extracted transition metal phosphate for enhanced OER activity
Beyond transition metal oxide, lithium tuned transition metal phosphates also demonstrated super catalytic activity over water oxidation (Figure 2). By continuously extracting lithium ions out of lithium transition metal phosphates, the materials exhibited significantly enhanced water oxidation catalytic activity. Particularly, the electrochemically delithiated Li(Ni,Fe)PO₄ nanoparticles anchored on reduced graphene oxide sheets afforded outstanding performance, generating a current density of 10 mA cm⁻² at an overpotential of only 0.27 V for over 24 h without degradation in 0.1 M KOH, outperforming the commercial precious metal Ir catalysts[26].
In situ electrochemical transformation from metal sulfides to metal oxides for OER

Figure 3 Schematic illustration of the synthesis process of ECT-TMOs and their corresponding morphology and Electrochemical performance of TMOs and ECT-TMOs in alkaline 1 M KOH solution. (a) Carbon fiber cloth substrate. (b) Pristine TMOs coated on CFC by the one-step electrochemical deposition. (c) TMSs obtained by the sulfurization treatment of the pristine TMOs. (d) ECT-TMOs formed by the in situ electrochemical oxidation tuning of TMSs. (e–h) SEM images of CFC, CoO, CoS₂, and ECT-CoO respectively. Scale bars: (e) 200 μm; (f–h) 500 nm. (i) The first three cyclic voltammetry curves of CoS₂ and Co₀.₃₇Ni₀.₂₆Fe₀.₃₇S₂ and (j) pristine CoO and Co₀.₃₇Ni₀.₂₆Fe₀.₃₇O, respectively. The curves were not applied to iR correction. (k) Polarization curves of pristine TMOs and ECT-TMOs as comparison, respectively. The curves were iR corrected. Summary of (d) overpotential at 10 mA cm⁻² of pristine TMOs and ECT-TMOs, respectively.

Besides lithium tuning, we also developed a novel in situ electrochemical oxidation tuning approach to develop a series of binary, ternary, and quaternary transition metal (e.g., Co, Ni, Fe) oxides from their corresponding dichalcogenides as highly active catalysts for much enhanced water oxidation (Figure 3). The electrochemically tuned cobalt-nickel-iron oxides grown directly on the three-dimensional carbon fiber
electrodes exhibit a low overpotential of 232 mV at current density of 10 mA cm\(^{-2}\), small Tafel slope of \(~37.6\) mV dec \(^{-1}\), and exceptional long-term stability of electrolysis for over 100 h in 1 M KOH alkaline medium, superior to most non-precious oxygen evolution catalysts reported so far. The materials evolution associated with the electrochemical oxidation tuning is systematically investigated by various characterizations, manifesting that the improved activities are attributed to the significant grain size reduction and increase of surface area and electroactive sites. This work provides a promising strategy to develop electrocatalysts for large-scale water-splitting systems and many other applications\[27, 28\].

*Lattice strain tuning via Li electrochemical tuning of battery electrode materials*

![Diagram](image)

**Figure 4** Schematic of the lattice constant change of LiCoO\(_2\) (LCO) substrates and how the lattice strains are induced to Pt NPs. (a) Pristine LCO shows a Co-O layer spacing of 4.69 Å. By electrochemically extracting half of the Li ions out, the layer spacing is increased to 4.82 Å along with the lattice tension of the Pt NPs outside. (b) LCO is first delithiated into L\(_{0.5}\)CO with layers expanded and then coated with Pt NPs. By intercalating back those Li ions, the Co-O layer spacing is decreased so as to induce compression on Pt NPs. The orientation of Pt NP is set to be different from (a) as a suggestion of non-epitaxial ALD growth. (c) The XRD peak shifts of LCO (003) represent the tensile and compressive strain induced to Pt NPs coated on these substrates.

In addition to Li electrochemical tuning method for significantly changed catalytic activities, lattice strain is another powerful tool to control the electronic structure of
catalysts and thus improve their performances. Lattice strain, either compressive or tensile, can alter the surface electronic structure by modifying the distances between surface atoms and in turn catalytic activity.[29] For platinum (Pt), previous studies have suggested that the 5d-band center of Pt can be shifted by ~0.1 eV with only 1% lattice strain[30], which can appreciably strengthen or weaken bonding of reaction intermediates to the surface. Inspired by Li ion battery research where the battery electrode materials usually undergo significant volume changes during charging or discharging processes. This is a major reason why battery finally fails after many cycles due to the electrode damage under repeated volume expansion and compression. However, this disadvantage in battery research becomes a great opportunity in catalysis to introduce lattice strain. When Li ions are electrochemically intercalated into or extracted out of electrode materials such as graphite, transition-metal dichalcogenides, silicon, or Li metal oxides, the volume and lattice spacing change from several percent to several fold[30]. For example, the Si electrode can expand up to four times its original size when fully lithiated to Li4.4Si, and LiCoO2 (LCO) undergoes ~3% volume changes during charge and discharge. This smaller value is still sufficient to generate strain that can alter catalysis. Li ions are sandwiched by Co-O octahedra slabs in LCO, and during charging, half of the Li\(^{+}\) are extracted to form Li\(_{0.5}\)CoO\(_2\) (L\(_{0.5}\)CO). The Co-O slabs with negative charge experience stronger electrostatic repulsions from each other, which increases the layer spacing (Figure 4a). When Li\(^{+}\) intercalates back during discharge, the lattice returns to its original spacing (Figure 4b). The successful and reversible delithiation and lithiation processes are reflected in the X-ray diffraction (XRD) patterns, as shown in Figure 4c.
Figure 5 High-resolution TEAM images of pristine and strained Pt NPs with (111) lattice compression and tension. Compression, (a) to (d); tension, (e) to (h). (a and b) TEAM images of $L_0.5\text{CO-Pt}$ and $L_0.5\text{CO-Pt}_T$. The red and yellow bars denote the areas we analyzed for (111) spacing. (c) The integrated pixel intensities of pristine and compressed Pt along (111) spacing directions (which is perpendicular to the facets). The peaks and valleys represent the atoms and gaps, respectively. The spacing of Pt (111) facets is averaged over six atomic layers for high accuracy. The pristine (111) is measured to be 2.29 Å, whereas the constrained (111) shows only 2.18 Å. (d) The bottom layers of pristine and compressed Pt (111) lattice fringes are aligned for the direct evidence of lattice constraint. The top atomic layer of compressed Pt locates at a much lower position than the pristine one. (e and f) TEAM images of LCO-Pt and LCO-Pt$_T$. (g) More than 5% tensile strain is observed with an increased (111) spacing of 2.42 Å. (h) A direct evidence of tensile strain with the top atomic layer of LCO-Pt$_T$ much higher than that of LCO-Pt. (a), (b), (e), and (f) share the same scale bar, and (d) and (h) share the same scale bar.
Figure 6  (a) The ORR polarization curves $L_{0.5}\text{CO-Pt}$, $L_{0.5}\text{CO-PtC}$, LCO-Pt, and LCO-Pt under 1600 rpm. The pristine Pt NPs on LCO and L$_{0.5}$CO substrates show negligible differences in ORR activity. Compressive strain shows an improved ORR activity, and tensile strain shows a decreased one. (b) The comparison of ORR activities under 0.84 V versus RHE. The error bars are based on at least three identical samples for each condition. (c) Illustration of the limiting potential “volcano” as a function of the change in $\Delta\text{GOH}$. The UL improved with increasing compressive strain and the intermediate strains are $\pm$2 and $\pm$4%. (d) Comparisons between the change in experimental half-wave potential and the change in theoretical overpotential caused by strain.

To introduce lattice strain on Pt catalysts with LCO as the tunable support, small Pt NPs (~5 nm) were deposited onto the surface of LCO or L$_{0.5}$CO particle supports (~500 nm) using atomic layer deposition method. By controlling the charging or discharging states of the substrate, we directly observed ~5% compressive and tensile strain on Pt (111) facets using transmission electron aberration-corrected microscopy (TEAM) in individual particles (Figure 5a, b, e and f).[31] To have an intuitive understanding of how much the lattice strain is, we aligned the (111) atomic layers (Figure 5c, d, g and h). After five layers of accumulation in spacing differences, the top layer of compressed Pt locates to a much lower position than that of the pristine Pt, and that of the expanded Pt locates to a much higher position, offering direct evidence of the lattice strain.

The ORR catalytic activities of Pt NPs in alkaline solution were tuned over a wide range, achieving nearly 90% improvement or more than 40% decrease in activity under compressive and tensile strain, respectively, as shown in Figure 6a and b. Density functional theory (DFT) calculations suggest that the UL which is determined as the required potential to make all steps in the pathway exergonic can be increased
and decreased by lattice compression and tension (Figure 6c), respectively. Moreover, the experimental half-wave potentials and theoretical limiting potentials for the strained and unstrained Pt catalysts are presented in Figure 6d with qualitative agreement. Given the wide variety of tunable battery electrode materials in existence, and the vast number of catalysts and reactions that can be improved with strain, this work demonstrate a highly general approach for studying these effects in the design of new catalytic materials.

**Shifting semiconductor/water interface energy levels via atomic dipoles**

Semiconductor/solution band edge alignment is a critical parameter governing the efficiency of solar-hydrogen generation from water. However, the specific adsorption of water at the semiconductor surface prohibited modulation over large magnitude. By introducing a strongly ionic dipole layer protected from direct contact with water, we successfully demonstrate the capability to control the band edge alignment over unprecedented range. Atomic scale controlled epitaxial SrTiO$_3$ (protective cap)/LaAlO$_3$ (dipole layer)/Nb-SrTiO$_3$ (001) (semiconductor) heterostructures were fabricated by pulsed laser deposition and the band edge shift was revealed from standard photoelectrochemical measurements in base. The effectiveness of the dipole was further confirmed by forming all-solid state Schottky junctions using Pt top contact giving quantitative consistency. The ability to manipulate interface energy levels free from materials specific constraints, such as electron affinity and surface chemical stability, has significant implications in solar-hydrogen generation, providing new design strategy to increase its efficiency.

**Figure 7** (a) Schematic of the dipole-engineered photoelectrode structure. The two polar surfaces of LaAlO$_3$ form a dipole effectively modulating the oxide/liquid band edge alignment. $E_C$ and $E_V$ corresponds to the conduction band bottom and the valence band maximum of the Nb:SrTiO$_3$, respectively. (b) Flatband potential ($E_{fb}$) shifting over 1 V by insertion of a sub-surface dipole layer, LaAlO$_3$. The similar shift observed in the built-in potential ($V_{bi}$) and the constant cap-SrTiO$_3$ barrier height ($\Phi_{PBE}$) on solid-state devices further proves the robust nature of the sub-surface dipole formation.
We have developed a new OER catalyst showing record-breaking activity with high stability in acid. By electrochemically treating an epitaxial SrIrO$_3$ thin film under positive bias in strong acid, a few atomic layers of Sr-ions in SrIrO$_3$ leaches out into the solution and the film surface transforms into an active OER catalyst reaching an overpotential smaller than 300 mV, substantially lower than any existing acid-stable OER catalyst. This active state was preserved for more than 30 hours showing its high potential in applications. Furthermore, we have proposed several surface atomic structures responsible for its high performance using theoretical calculations, strategically guiding experiments towards identification of active sites and further enhancing its performance. Given the smaller loading of iridium required compared to the existing iridium-based catalysts, this study has set a pathway to boost the electrochemical production of hydrogen and carbon-based fuels.

Conclusions

Based on the significant results we achieved above, we found that the potential needed for overall water splitting at 100 mA cm$^{-2}$ using our bifunctional ultra-small NiFeO$_x$ nanoparticles is $\sim$1.73 V, which is smaller than that for the combination of Pt/C and Ir/C catalysts ($\sim$1.86 V). So we not only reduce the cost for water splitting system by eliminating the precious metals, but also save $\sim$7.5% total energy for hydrogen production in water-alkali industry, which means $\sim$7.5% reduction in emissions of greenhouse gases.

Moreover, this project supported by GCEP mainly focus on exploring highly efficient and robust electrocatalysts aiming at reducing the barriers as well as promoting the important electrochemical reactions. Satisfied electronic structures of the electrocatalysts are highly required with proper binding energies towards the reactants, intermediates, and the products. The lithium ion batteries (LIBs) technology has been maturely developed in the past few decades, and various materials whose electronic structures can be changed by reacting with lithium have been screened with their potentials for LIBs. In addition, the LIBs technology offers a large thermodynamic potential range for continuous tuning the electronic structures, thus may open up new possibilities to exploring better electrocatalysts.

4 types of strategies to tune the existing materials are demonstrated for achieving better electrochemical performances. 1) The sizes of transition metal oxides were greatly reduced to several nanometers by cycling with lithium, and the nanoparticles showed extraordinary bifunctional activity for overall water splitting. 2) Extracting Li out of the lithium containing cathode materials (e.g. lithium transition metal phosphates) dramatically improved their corresponding electrocatalytic activities. 3) We observed an in situ electrochemical transformation of transition metal sulfides to their corresponding oxides for better OER activities. 4) The Pt lattice strain has been flexibly tuned by Li electrochemical tuning of LCO for better ORR catalysis. The diversity and generality have made this electrochemical tuning methodology as a
powerful approach to explore advanced catalysts. Thus, this approach should be paid much more attention as it can also play an important role for the afore-mentioned electrochemical reactions, resulting in efficient utilization of energy as well as reducing the greenhouse gases emissions.

**Publications and Presentations**

**Publications**


**Presentations**


**Contacts**

Prof. Yi Cui: yicui@stanford.edu
Prof. Harold Hwang: hyhwang@stanford.edu