Non-Fermi Liquids as Highly Active Oxygen Evolution Reaction Catalysts

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The oxygen evolution reaction (OER) plays a key role in emerging energy conversion technologies such as rechargeable metal-air batteries, and direct solar water splitting. Herein, a remarkably low overpotential of ≈150 mV at 10 mA cm⁻² in alkaline solutions using one of the non-Fermi liquids, Hg₂Ru₂O₇, is reported. Hg₂Ru₂O₇ displays a rapid increase in current density and excellent durability as an OER catalyst. This outstanding catalytic performance is realized through the coexistence of localized d-bands with the metallic state that is unique to non-Fermi liquids. The findings indicate that non-Fermi liquids could greatly improve the design of highly active OER catalysts.

The complex oxygen evolution reaction (OER) is the crux of emerging energy conversion technologies like metal-air batteries[1,2] and direct solar water splitting.[3,4] Although catalysts based on perovskites,[5–9] oxy-hydroxides,[10,11] RuO₂ and IrO₂,[12] display high current densities and facilitate the reaction, most of them have room for improvement in their overpotentials and conversion efficiencies. Here, a remarkably low overpotential of ≈150 mV at 10 mA cm⁻² in alkaline solutions is reported for OER using one of the non-Fermi liquids (with anomalous metallic state caused by strong electron–electron interactions), Hg₂Ru₂O₇. Hg₂Ru₂O₇ displays a rapid increase in the current density and an excellent durability as an OER catalyst. This outstanding catalytic performance is realized through the coexistence of localized d-bands with the metallic state of the non-Fermi liquid. The findings indicate that non-Fermi liquids could greatly improve the design of highly active OER catalysts.

Recent reports[5–10] on bulk electronic states of transition metal ions manifesting on the catalyst surface have greatly advanced our understanding of OER catalysts. Through their evaluation of OER activities on insulating AMO₃ perovskite oxides, Suntivich et al.[9] suggested that catalysts exhibit maximum OER activity when the number of d-electrons in the e₈g orbital was near unity for transition metal ions occupying the octahedral sites.[5] Since the d-bonding e₈g orbital has stronger overlap with adjacent O 2p orbitals of oxygen adsorbates, electron transfer between the M-cation and OER intermediates is faster. For insulating AMO₃ perovskite oxides, the unoccupied e₈g level in the 3d conduction band is lowered by the applied overpotential (η) in order to overlap with the O 2p band of oxygen adsorbates (Figure 1a). The gap (Δ₉) between the O 2p valence band and the unoccupied 3d conduction band can then be treated as a measure of overpotential, or as a direct proxy of the OER activity. This gap is caused by the on-site Coulomb potential U₀d (Figure 1) that localizes the d-bands. When the gap is small, the overpotential and corresponding Tafel slope[11,14] are also small, leading to rapid electron transfer between the M-cation and the oxygen adsorbates. In general, insulating perovskite oxides have high OER activity, but require high overpotentials due to the wide gap between the O 2p valence band and the unoccupied 3d conduction band. One solution is to design a catalyst composed of several transition metals with multiple OER active sites. As for gelled FeCoW oxyhydroxide[10] such a design can sometimes greatly enhance the catalytic activity through synergistic interplay between transition metals. However, the large gap between the O 2p valence band and the unoccupied 3d conduction band still leads to a substantial overpotential.
in detail. \( \text{Hg}_2\text{Ru}_2\text{O}_7 \) (Ru\(^{3+} \) : 4d, \( t_{2g} \), \( e_g \)) undergoes a metal–insulator transition at 108 K.\(^{[19–21]} \) However, the localized d-bands of the Mott–Hubbard\(^{[24]} \) insulator (Figure 1a) are retained across the transition\(^{[22]} \) and the system adopts a non-Fermi liquid state above 108 K\(^{[22, 23]} \) (Figure 1b). Non-Fermi liquid systems are d- or f-electron systems characterized by strong electron–electron interactions that prevent entry into the Fermi liquid ground state\(^{[18]} \) and some of them exhibit superconductivity\(^{[25, 26]} \). The fascination with the physics of non-Fermi liquids is the unusual temperature dependence of their physical properties\(^{[17, 18, 27]} \). For example, the electrical resistivity \( \rho \) of \( \text{Hg}_2\text{Ru}_2\text{O}_7 \) increases proportionally to \( T \) above 108 K\(^{[19–21, 23]} \) instead of \( T^2 \) as in Fermi liquids.

The catalytic OER activity of the non-Fermi liquid \( \text{Hg}_2\text{Ru}_2\text{O}_7 \) was studied in comparison with \( \text{Ca}_2\text{Ru}_2\text{O}_7 \),\(^{[28]} \) \( \text{Cd}_2\text{Ru}_2\text{O}_7 \),\(^{[29]} \) and \( \text{RuO}_2 \) on glassy carbon disk electrodes. The OER measurements were conducted in 0.1 m KOH aqueous solutions and the current densities were normalized to the glassy carbon disk electrode area. \( \text{Hg}_2\text{Ru}_2\text{O}_7 \) was confirmed to be single-phase with the pyrochlore structure (Figure 2) by synchrotron X-ray diffraction (see the XRD profile in Figure S1, Supporting Information). Also, the Ru\(^{3+} \) valence in this compound was confirmed by X-ray photoemission spectra (see the Ru 3d\(^{3/2} \) peak in Figure S8, Supporting Information). \( \text{Hg}_2\text{Ru}_2\text{O}_7 \) particles are in the size of 1–5 \( \mu \)m (see the scanning electron microscopy (SEM) image in Figure S2, Supporting Information).

Figure 3a shows the capacitance-corrected voltammograms for the isostructural \( \text{Hg}_2\text{Ru}_2\text{O}_7 \), \( \text{Ca}_2\text{Ru}_2\text{O}_7 \), and \( \text{Cd}_2\text{Ru}_2\text{O}_7 \). The OER activity of \( \text{Hg}_2\text{Ru}_2\text{O}_7 \) is significantly larger than other cubic pyrochlore ruthenates. At an applied potential of 1.5 V versus RHE a current density of \( \approx 400 \) mA cm\(^{-2} \) was recorded for \( \text{Hg}_2\text{Ru}_2\text{O}_7 \) (Figure 3b), which is comparable to gelled nano-porous FeCoW oxy-hydroxide (we note that the mass loading of FeCoW oxy-hydroxide is much larger than \( \text{Hg}_2\text{Ru}_2\text{O}_7 \)).\(^{[10]} \) Since high OER activity was also reported for \( \text{Pb}_2\text{Ru}_2\text{O}_{6.5} \) and \( \text{Bi}_{3.4}\text{Ru}_4\text{O}_7 \) pyrochlore oxides by Parrondo et al.,\(^{[30]} \) catalysts with pyrochlore structure are potentially highly active OER catalysts apart from the well-known perovskite oxides.\(^{[5, 6]} \) The mass OER activity of \( \text{Hg}_2\text{Ru}_2\text{O}_7 \) at 1.5 V versus RHE is \( \approx 400 \) mA mg\(^{-1} \), while that of \( \text{Pb}_2\text{Ru}_2\text{O}_{6.5} \) is \( \approx 200 \) mA mg\(^{-1} \).\(^{[30]} \) Figure 3c–e shows the \( iR \)-corrected Tafel slopes obtained under steady-state conditions. All tested cubic pyrochlore ruthenates exhibited two Tafel slopes (Figure 3c–e). The two clear Tafel slopes in Figure 3c–e may suggest a similar switch in the rate-determining step for OER at \( \approx 1.52 \) V as noted for \( \text{RuO}_2 \).\(^{[31]} \) However, the absolute value of the Tafel slope was not used to determine the reaction step (in the OER) due to the delicate use of the Tafel equation as pointed out by Gileadi and Kirowa-Eisner.\(^{[32]} \) The smaller
Tafel slope in Figure 3c together with the lower onset potential demonstrates that Hg$_2$Ru$_2$O$_7$ exhibits higher OER activity than other cubic pyrochlore ruthenates. Although the temperature dependence of the electrical resistivity of Ca$_2$Ru$_2$O$_7$ (Ru$^{4+}$: 4d, t$_{2g}^3$ e$_g^0$) and Cd$_2$Ru$_2$O$_7$ (Ru$^{4+}$: 4d, t$_{2g}^3$ e$_g^0$) resembles an insulator (the d-bands are gapped), their electrical resistivity at room temperature (2–5 mΩ cm) is comparable to metals [28, 29]. As stated by Miyazaki et al. [33], the metal–insulator transition of Ca$_2$Ru$_2$O$_7$ and Cd$_2$Ru$_2$O$_7$ is suppressed to a small anomaly at ≈25 and ≈30 K in sharp contrast with Hg$_2$Ru$_2$O$_7$. This suggests that the metallic states in Ca$_2$Ru$_2$O$_7$ and Cd$_2$Ru$_2$O$_7$ are suppressed in comparison with Hg$_2$Ru$_2$O$_7$. Since the electronic bands in Figure S7 (Supporting Information) are composed of Ru 4d-electrons, the localized d-bands of Ca$_2$Ru$_2$O$_7$ and Cd$_2$Ru$_2$O$_7$ are wider due to the narrower metallic states. Accordingly, the reason why Cd$_2$Ru$_2$O$_7$ (Figure 3e) has a lower OER activity than Ca$_2$Ru$_2$O$_7$ is likely to be the wider d-band and the narrower metallic state (Figure S7, Supporting Information).

Figure 4 compares the overpotential of Hg$_2$Ru$_2$O$_7$, Ca$_2$Ru$_2$O$_7$, Cd$_2$Ru$_2$O$_7$, and RuO$_2$ with other highly active oxide OER catalysts [5, 6, 9, 10, 30, 34]. Here, the overpotential of Hg$_2$Ru$_2$O$_7$ (η = 150 mV at 10 mA cm$^{-2}$) is superior to other highly active OER catalysts (e.g., NiFeOOH [34]) and it is the lowest OER overpotential for oxide catalysts in alkaline solutions reported to date. Also, Hg$_2$Ru$_2$O$_7$ outperforms among the Ru-based catalysts, showing the lowest overpotential and the highest TOF (see the OER activity in Table S6, Supporting Information). Furthermore, the overpotential of Hg$_2$Ru$_2$O$_7$ is 174(8) mV at 20 mA cm$^{-2}$ and 269(16) mV at 100 mA cm$^{-2}$, exhibiting the comparable values with state-of-the-art OER catalysts including oxygen-incorporated Ni$\text{Fe}_x$$\text{S}^{15}$ (259 mV at 20 mA cm$^{-2}$) and Ni$\text{Fe}_x$$\text{O}_y$$\text{NiOOH}^{16}$ (270 mV at 100 mA cm$^{-2}$). The low overpotential and a small Tafel slope can be rationalized in terms of the electronic structure of Hg$_2$Ru$_2$O$_7$ (Ru$^{4+}$: 4d, t$_{2g}^3$ e$_g^0$) where the localized d-band coexists with the metallic state (Figure 1b). Here, the Hg 5d states (binding energy: 6–12 eV)
do not contribute to OER since their d-levels are distributed far away from the Fermi level.\[22\] Also, any correlation between structural differences and the catalytic activity can be neglected since the bond distances and bond angles of the cubic pyrochlore ruthenates are almost identical (see the crystallographic data in Table S1, Supporting Information). Since the metallic state exists between the localized d-bands, the unoccupied eg level at the Fermi level is lowered by the overpotential and overlaps with the O 2p band of the oxygen adsorbates (Figure 1b). In this way, the electron transfer between the Ru eg orbital and the O 2p orbital of the oxygen adsorbates becomes rapid. In summary, all these figures of electrochemical properties (Figures 3 and 4) demonstrate that the OER performance of Hg2Ru2O7 outperforms among the existing oxide OER catalysts.

Extended electrochemical studies were conducted to investigate the catalytic stability of Hg2Ru2O7. The chronoamperometric curve in Figure 5a shows that the OER activity of Hg2Ru2O7 is stable in 0.1 M KOH with the current density (at a constant voltage of 1.5 V vs RHE) sustaining ≈95% of the initial value even after 100 h, while the current density of Ca2Ru2O7 decreases down to ≈59% of the initial value after 100 h. The catalytic stability of Hg2Ru2O7 was also tested in 1.0 and 6.0 M KOH electrolyte, exhibiting excellent stability of ≈95% regardless of the KOH molarity (Figure S11, Supporting Information). Figure 5b shows the voltammograms of Hg2Ru2O7 and Ca2Ru2O7 over 50–100 cycles. The current density of Ca2Ru2O7 decreases with cycle number, while that of Hg2Ru2O7 increases due to the slight progression of amorphization. Therefore, Figure 5a,b demonstrates that Hg2Ru2O7 possesses an OER stability comparable to the very stable CaCu3Fe4O12.\[6\] The stability of Hg2Ru2O7 was further probed using high-resolution transmission electron microscopy (HRTEM) both before and after 50 or 100 OER cycles. Figure 5c,d shows the HRTEM and fast Fourier
transform (FFT) images of Hg$_2$Ru$_2$O$_7$ and Ca$_2$Ru$_2$O$_7$ before and after OER measurements. Before getting into detail about the catalytic stability, we note that Hg$_2$Ru$_2$O$_7$ is a non-Fermi liquid, while Ca$_2$Ru$_2$O$_7$ is in the vicinity of a metal and an insulator. The electrical resistivity of Hg$_2$Ru$_2$O$_7$ (at room temperature) is in the range of a metal,[19,20] and its temperature dependence is characteristic to non-Fermi liquids.[19,20] On the other hand, the electrical resistivity of Ca$_2$Ru$_2$O$_7$ (at room temperature) is in the range of a metal,[28] while its temperature dependence resembles that of an insulator[28] (suggesting the existence of a band gap). Also, as reported by Yagi et al.[6] and May et al.,[37] the catalytic activity of an OER catalyst is determined by the crystalline layer and amorphous layer remains almost constant (≈5 nm) of the amorphous layer (the thickness ratio between the crystalline layer and amorphous layer is small even after 100 cycles (Figure 5c). However, after casting, an OER measurement starts with a similar surface state for Hg$_2$Ru$_2$O$_7$ and Ca$_2$Ru$_2$O$_7$. Ca$_2$Ru$_2$O$_7$ possesses highly crystalline surface structures. However, after casting, ≈5 nm amorphous layer is immediately formed on their catalytic surface (Figure 5c,d). In other words, the OER measurement starts with a similar surface state for Hg$_2$Ru$_2$O$_7$ and Ca$_2$Ru$_2$O$_7$. However, there is a clear difference between Hg$_2$Ru$_2$O$_7$ and Ca$_2$Ru$_2$O$_7$ in their cycle dependence toward the OER measurement (Figure 5b). The current density for Hg$_2$Ru$_2$O$_7$ gradually increases with cycling up to cycle 100, while that for Ca$_2$Ru$_2$O$_7$ clearly decreases with cycling after cycle 10. This contrast can be attributed to the difference of the amorphous layer thickness after multiple cycling (Hg$_2$Ru$_2$O$_7$: ≈5 nm after 100 cycles, Ca$_2$Ru$_2$O$_7$: ≈25 nm after 50 cycles). As reported by May et al.,[37] amorphization gradually increases the electrochemically active surface area of the catalyst. On the other hand, the electrical resistivity increases with amorphization (which leads to the decrease of the OER current density) due to the lattice irregularity of the amorphous layer. We note that the initial electronic bands (near the Fermi level) of the crystalline layer are maintained in the amorphous layer and the surface electronic structure is analogous to the bulk electronic structure. Therefore, the lattice irregularity of the amorphous layer not only increases the electrical resistivity, but it also leads to the increase of the band gap in the case of Ca$_2$Ru$_2$O$_7$ due to its insulating character of the temperature dependence.[28] In the case of Hg$_2$Ru$_2$O$_7$, the growth of the amorphous layer is small even after 100 cycles (Figure 5c).

**Figure 4.** OER overpotentials of cubic pyrochlore ruthenates and other highly active oxide (and oxy-hydroxide) OER catalysts. The overpotential (η) at the geometric current density of 10 mA cm$^{-2}$ was determined by η = E + 1.23 V. All the catalysts here have small Brunauer–Emmett–Teller (BET) surface areas, and their current densities were normalized to the glassy carbon disk electrode area instead of the BET surface area. Since OER measurements for these catalysts were conducted in KOH solutions, the overpotentials are compared to those of NiFeOOH (Batchellor and Boettcher[34]), RuO$_2$ (this study), CCFO (Yagi et al.[6]), and Bi$_2$Ru$_2$O$_7$ (Parrondo et al.[30]) under controlled conditions.

The diffused Hg$^{2+}$ provided by the crystalline layer thus reaches the outermost surface after 100 OER cycles due to the thin amorphous layer of ≈5 nm and finally dissolves in the alkaline solution (see the compositional information in Table S4 (Supporting Information)) determined by the integrated XPS peak areas in Figure S9, Supporting Information). Therefore, the electrochemically active surface area slightly increases and the electrical resistivity does not increase due to the almost constant thickness (≈5 nm) of the amorphous layer (the thickness ratio between the crystalline layer and amorphous layer remains almost constant at the ≈10 nm catalytic surface). For this reason, the OER current density of Hg$_2$Ru$_2$O$_7$ slightly increases with cycling. We also note that the dissolved Hg$^{2+}$ in the alkaline solution (Table S4, Supporting Information) does not alter the initial electronic structure since the electronic bands (near the Fermi level) are merely composed of the Ru 4d-electrons. In the case of Ca$_2$Ru$_2$O$_7$, the growth of the amorphous layer was ≈20 nm (Figure 5d after 50 cycles), so the ≈10 nm catalytic surface is merely composed of the amorphous layer and the electrical resistivity increases rapidly, totally exceeding the increase in electrochemically active surface area. Therefore, the OER current density of Ca$_2$Ru$_2$O$_7$ starts to decrease after cycle 10 and becomes less than half at 1.5 V versus RHE for cycle 50 (at cycle 10, the increase of the electrochemically active surface area cancels out the increase of the electrical resistivity). We note that the chemical analysis via XPS (Table S4, Supporting Information) suggests that the diffused Ca$^{2+}$ continuously provided by the crystalline layer did not reach the outermost surface due to the thick amorphous layer of ≈25 nm. The competition between the increase in electrochemically active surface area and increase in the electrical resistivity was also described by Yagi et al.[6] comparing the stable CCFO after 100 OER cycles (with an amorphous layer of ≈5 nm corresponding to Hg$_2$Ru$_2$O$_7$ in our study) with the unstable CFO after 100 OER cycles (with an amorphous layer of ≈20 nm corresponding to Ca$_2$Ru$_2$O$_7$ in our study). The difference of the extent of amorphization in Hg$_2$Ru$_2$O$_7$ and Ca$_2$Ru$_2$O$_7$ during the OER can be explained by bonding strength as demonstrated by Yagi et al.[6] Hg$_2$Ru$_2$O$_7$ has a strong covalent bonding network.
In conclusion, the non-Fermi liquid Hg$_2$Ru$_2$O$_7$ exhibited the lowest reported OER overpotential for oxide catalysts (≈150 mV at 10 mA cm$^{-2}$ disk) in alkaline solutions with a rapid increase in the current density and excellent catalytic stability. More importantly, this outstanding OER performance can be explained in terms of the coexistence of the localized d-bands and the metallic state in the material. These findings indicate that the principles of non-Fermi liquids could serve as new design criteria for highly active OER catalysts.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
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Conflict of Interest
The authors declare no conflict of interest.

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