



CaCu₃Ti₄O₁₂: A Bifunctional Perovskite Electrocatalyst for Oxygen Evolution and Reduction Reaction in Alkaline Medium



H.S. Kushwaha^a, Aditi Halder^b, P. Thomas^c, Rahul Vaish^{a,*}

^a School of Engineering, Indian Institute of Technology Mandi, Himachal Pradesh, India

^b School of Basic Sciences, Indian Institute of Technology Mandi, Himachal Pradesh, India

^c Dielectric Materials Division, Central Power Research Institute, Bangalore, India

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ABSTRACT

Perovskite oxides are prominent materials as the bifunctional electrocatalysts for both oxygen reduction/evolution reactions (ORR/OER) for the electrochemical energy conversion and storage using regenerative fuel cells and rechargeable metal-air batteries. In this work, a quadruple perovskite CaCu₃Ti₄O₁₂ has been synthesized oxalate precursor route. X-ray diffraction pattern shows phase purity of the synthesized electrocatalyst. The synthesized CCTO electrocatalyst have crystallite size of 26 nm. Electrochemical investigations reveal that CCTO exhibit efficient catalytic activity. More interestingly, an extremely high OER activity is observed for CCTO electrocatalysts which is found superior than similar class of perovskites. Additionally, CCTO shows efficient ORR activity with an onset potential of 0.83 V which is better than that of Pt/C catalyst (≈0.94 V). These results demonstrate the significant potential of CCTO perovskite as a bifunctional electrode material for alkaline fuel cells and metal-air batteries.

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1. Introduction

Oxygen electrochemistry based energy storage and harvesting devices like metal-oxygen batteries, fuel cells, and water splitting hydrogen production have potential to address global energy and environmental challenges [1–4]. Oxygen evolution (OER) and oxygen reduction reaction (ORR) are main electrochemical processes that govern an extensive range of electrochemistry based energy conversion and storage devices [5–7]. In most of the processes, electrocatalytic water splitting is performed in alkaline medium besides acidic electrolytes because of the cost effective fabrication and less vulnerability to electrode corrosion [8,9]. However, the efficiency of these systems has been severely restricted by the stagnant kinetic reactions involves in the OER and ORR [10,11]. Nobel metal based electrocatalysts such as Pt, IrO₂ and RuO₂ are conventionally used as an electrode material, but the rareness, high cost, and poorer stability of precious group metal (PGM) catalysts have prohibited the extensive and significant applications of electrochemical devices [1,12–17]. Pt shows insufficient OER catalytic activity because of the transformation

in the insulating platinum oxides during electrocatalysis, whereas RuO₂ is not stable at higher overpotentials due to the conversion in higher-valent ruthenium oxides [18]. IrO₂ is considered as the most efficient catalyst so far for OER, but have poor performance for ORR [19]. However, it is not easy to achieve efficient bifunctional catalytic activities with the same catalyst for oxygen reactions. The major challenge in renewable electrochemical system is to fabricate economically viable, earth-abundant, low-cost, competent catalysts for the OER and ORR. In plant species, water splitting is executed via the water-plastoquinone oxidoreductase which contains CaMn₄O_x clusters to enhance water oxidation at lower overpotentials [20,21]. Though, it is not possible to use natural catalyst in industrial electrochemical systems due to lack of stability during electrochemical reactions. Therefore, it is highly desirable to synthesize cost effective non-PGM bifunctional catalysts with efficient catalytic activity and high stability for both ORR and OER, but it remains a intimidating scientific challenge.

ABO₃ perovskite oxide has gained significant attention because of their high electrocatalytic activities. Some of the perovskite catalysts have matched or even higher catalytic performance than the noble metal oxide catalysts such as IrO₂ and RuO₂ [22–26]. Perovskites oxides have ABO₃ structure, where A site is occupied by the rare-earth or alkaline earth element and B is occupied with a

* Corresponding author. Phone: +91-1905-237921, Fax: +91-1905-237945.

E-mail addresses: rahul@iitmandi.ac.in, vaish.rahul@gmail.com (R. Vaish).

transition metal. Perovskite catalysts have great structural/chemical flexibility that may enhance electrochemical performance. Several studies have been performed to investigate the OER and ORR mechanism for the perovskites electrocatalysts. Suntivich et al. proposed that the better catalytic activity can be achieved for OER by using the B-site transition metals which have e_g occupancy close to unity. In ABO_3 perovskite, covalency among the metal 3d orbital and oxygen 2p orbitals in transition metal–oxygen complex at B-site governs the catalytic by improving the charge transfer in the rate-determining steps (RDS) [27–29]. However, in case of perovskite catalysts, this is not universally true because most of the perovskite catalysts show activity only for the OER, but inactive for the ORR. Oxygen vacancies in perovskite catalysts also play an important role to determine OER/ORR performance[30,31]. The oxygen vacancies in ABO_3 catalysts can contribute as donors or acceptors during electrocatalysis to increase the charge transfer between adsorbed species and catalyst surface. Intrinsic ORR/OER activities in oxygen deficient oxides were observed due to simultaneous creation and filling oxygen vacancies[32]. Recently, Grimaud et al. reported that double perovskites show higher catalytic performance due to the presence of oxygen vacancies. The oxygen vacancies stabilize the d_{xz} , d_{yz} and d_z^2 molecular orbitals in the parentage orbitals t_{2g} and e_g , respectively and creates an oxygen-deficient octahedral symmetry[23]. $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-d}$ (BSCF82), $Ba_{0.5}Sr_{0.5}Co_{0.4}Fe_{0.6}O_{3-d}$ (BSCF46) and $SrCo_{0.8}Fe_{0.2}O_{3-d}$ (SCF82) have been extensively explored because of their better OER activities, but surface amorphization of these catalysts during OER cycles decreases their stability[22,23,27,33,34]. Hence, it is essential to deal with both the efficient catalytic activity and stability of electrode to develop an efficient catalyst.

$CaCu_3Ti_4O_{12}$ (CCTO) is a double-perovskite with cubic ($AA'BO_3$) structure which have Ca^{2+} and Cu^{2+} structured on the A and A' site, and Ti^{4+} ordered on the B site. The distorted TiO_6 octahedral forms a square planar structure to produce Jahn–Teller distortion in Cu^{2+} [35,36]. The extended structure incorporates Ti^{4+} and the open-shell Cu^{2+} within the perovskite without any doping, and both of the cations fill the specific sites within the crystal structure. Extensive investigations have been performed to analyze the physiochemical properties of $CaCu_3Ti_4O_{12}$ after the finding of its extraordinarily high dielectric constant, the cause of which is not fully understood until now[37,38]. However, it is not investigated now that whether CCTO have intrinsic or extrinsic properties in nature. In CCTO, every oxygen atom has strong covalence bonding

with $A'-Cu^{2+}$ ion and two $B-Ti^{4+}$ ions. Therefore, the charge transfer between $A'-Cu$ and $B-Ti$ ions plays main role in electrocatalytic activity[39–41]. The Cu (Ti) e_g and O 2p orbitals are highly overlapped in the square-planar (octahedral) coordination. It is reported that the visible light photocatalytic activity of CCTO is mainly governed by the complex covalent bonding network present in octahedral structure[35,36]. Further, to the best of our knowledge, Ti^{4+} -perovskites have not been explored as bifunctional electrocatalysts until now. In this report, we show that Cu^{2+} and Ti^{4+} based double perovskite CCTO exhibits bifunctional electrocatalytic activity, which is comparable to or exceeds that of state-of-the-art perovskite electrocatalysts like BSCF and the gold standard RuO_2 .

2. Experimental Details

2.1. Synthesis of $CaCu_3Ti_4O_{12}$

$CaCu_3Ti_4O_{12}$ (CCTO) electrocatalyst powder was synthesized using the oxalate precursor route as discussed in our previous reports [36,42].

2.2. Material Characterization

X-ray powder diffraction (XRD) studies were performed for as synthesized CCTO powder using an X'pert diffractometer (Philips, Netherlands) with Cu $K\alpha_1$ radiation ($\lambda = 0.154056$ nm) in a wide range of 2θ (10° – 90°) with 0.02 step size the structural properties and phase purity of synthesized catalyst. Surface morphology of synthesized catalyst was analysed using scanning electron microscope (JEOL SEM 5610).

2.3. Electrochemical Measurement

Electrochemical measurements for ORR and OER were carried out on an Autolab Electrochemical Workstation (Metrohm) in a three- electrode system using 0.1M KOH as the electrolyte. Rotating glassy carbon disk electrode (RDE) with a diameter of 5 mm was used as working electrode, Ag/AgCl as reference electrode and platinum wire as counter electrode. To prepare the ink for working electrode, 5 mg CCTO and 10 mg Vulcan XC-72 were dispersed in 2.5 mL distilled water and 2.5 mL isopropyl alcohol. 300 μ L Nafion solution (5 wt %) was also added. The whole

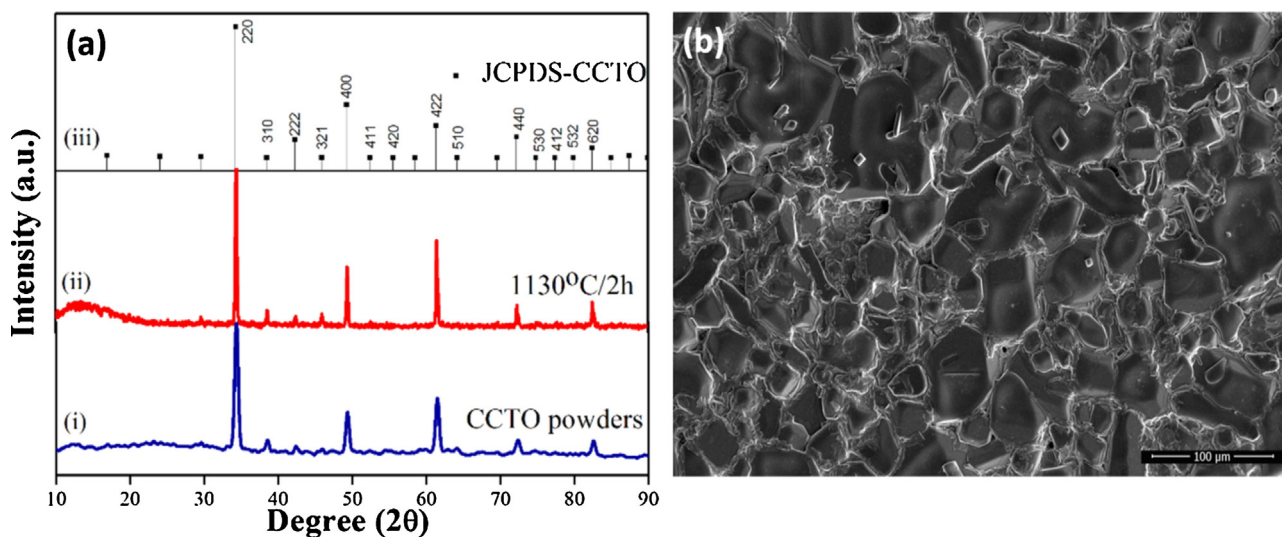


Fig. 1. (a). X-ray diffraction patterns of (i) as prepared $CaCu_3Ti_4O_{12}$ (CCTO), (ii) CCTO pellets sintered at $1130^\circ C/2$ h and (iii) ICDD data file card no. 01-075-1149 for CCTO. (b) Scanning electron micrograph of the CCTO pellet sintered at $1130^\circ C/2$ h.

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