**Study of fluorine doped (Nb,Ir)O₂ solid solution electro-catalyst powders for proton
exchange membrane based oxygen evolution reaction**

Karan Sandeep Kadakia^{1,#}, Prashanth H. Jampani^{2,#,*}, Oleg I. Velikokhatnyi^{2,3}, Moni Kanchan
Datta^{2,3}, Prasad Patel¹, Sung Jae Chung⁴, Sung Kyoo Park², James A. Poston⁵, Ayyakkannu
Manivannan⁵ and Prashant N. Kumta^{1,2,3,4,6}

¹Chemical and Petroleum Engineering, Swanson School of Engineering, University of
Pittsburgh, PA 15261.

²Bioengineering, Swanson School of Engineering, University of Pittsburgh, PA 15261.

³Center for Complex Engineered Multifunctional Materials, University of Pittsburgh, PA 15261.

⁴Mechanical Engineering and Materials Science, Swanson School of Engineering, University of
Pittsburgh, PA 15261.

⁵US Department of Energy, National Energy Technology Laboratory, Morgantown, WV 26507.

⁶Department of Oral Biology, School of Dental Medicine, University of Pittsburgh, PA 15217.

*Corresponding author: Prashanth Jampani Hanumantha (pjampani@pitt.edu)

Department of Bioengineering, 818 Benedum Hall, 3700 O'Hara Street, Pittsburgh, PA 15261.

Tel: +1-412-624-3376, Fax: +1-412-624-3699

[#]Contributed Equally

Article type: Regular Article

Abstract:

High surface area ($\sim 300 \text{ m}^2/\text{g}$) nanostructured powders of $(\text{Nb}_{1-x}\text{Ir}_x)\text{O}_2$ and $(\text{Nb}_{1-x}\text{Ir}_x)\text{O}_2:10\text{F}$ ($\sim 100 \text{ m}^2/\text{g}$) have been examined as promising oxygen evolution reaction (OER) electro-catalysts for proton exchange membrane (PEM) based water electrolysis. Nb_2O_5 and 10 wt.% F doped Nb_2O_5 powders were prepared by a low temperature sol-gel process which were then converted to solid solution $(\text{Nb},\text{Ir})\text{O}_2$ and 10 wt.% F doped $(\text{Nb},\text{Ir})\text{O}_2$ [$(\text{NbIr})\text{O}_2:10\text{F}$] electro-catalysts by soaking in IrCl_4 followed by heat treatment in air. Electro-catalyst powders of optimal composition $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2:10\text{F}$ with $\sim 75 \text{ at.}\%$ reduction in noble metal content exhibited comparable OER activity to commercial hydrated IrO_2 and nanostructured in-house chemically synthesized IrO_2 . The $(\text{Nb},\text{Ir})\text{O}_2:10\text{F}$ electro-catalyst demonstrated excellent long term structural/corrosion stability comparable to in-house chemically synthesized pure $\text{IrO}_2:10\text{F}$. First-principles calculations of the total energies, electronic structures and cohesive energies of the model systems have been performed and correlated to the excellent activity, long term stability of $(\text{Nb},\text{Ir})\text{O}_2:\text{F}$ for OER obtained experimentally.

Keywords:

PEM electrolysis; $(\text{Nb},\text{Ir})\text{O}_2:\text{F}$; oxygen evolution; nanoparticles; electro-catalysts

1. Introduction:

The gradual transition from carbon based fuels to a more ubiquitous power source such as hydrogen is widely seen as a viable long-term solution to meeting the growing global energy requirements and in order to avoid further anthropomorphic alteration of the earth's climate [1-5]. A hydrogen based energy system will be ideal for driving a variety of energy related devices in an efficient, clean and safe manner. However, two major hurdles exist, limiting commercialization (a) the ability to economically generate ultra-high purity hydrogen utilizing a carbon free method (b) safe and efficient hydrogen storage and distribution. Water electrolysis is an efficient path to hydrogen production [2, 3, 5-9] and has the advantages of no greenhouse gas emissions or toxic byproducts, especially when the current is supplied using sustainable, renewable energy sources. However, the capital costs associated with current electrolyzer technologies are a major barrier for attaining the targeted hydrogen production cost (\$2.00-\$4.00/gge) due to the use of noble metal based electro-catalysts namely, Pt, IrO₂ and RuO₂.

Use of corrosion resistant non-precious transition metal oxide catalysts such as niobium oxide (Nb₂O₅), tin oxide (SnO₂), tantalum oxide (Ta₂O₅) or titanium oxide (TiO₂) as electrodes with high activity and durability would decrease the overall capital costs. These non-noble metal oxides however do not show any catalytic activity for oxygen evolution reaction (OER) in PEM electrolysis conditions and at the same time exhibit very poor electronic conductivity which is a major detriment to achieving the desired optimal charge transport kinetics. It has been reported [10-20] that mixed noble-non-noble metal oxides [(IrO₂, RuO₂)-(Nb₂O₅, SnO₂, Ta₂O₅, TiO₂)] reduce the noble metal loading while facilitating the achievement of high electronic conductivity

and catalytic activity though reports have identified that there is a limiting concentration of diluents and support structures beyond which the active surface area, electrical conductivity and electrochemical activity decrease[11, 14, 16-19, 21-27]. Work from the present group of authors has demonstrated thin film solid solutions of F doped metal oxide ($M_xO_y:F$, $M=Sn, Nb, Ta$) containing low amount of IrO_2 or RuO_2 (~20 at.%) such as $(Sn, Ir)O_2:F$, $(Sn, Ru)O_2:F$, and $(Ta, Ir)O_2:F$ with electrochemical performance comparable to that of pure IrO_2 electro-catalyst[28-33]. Improvement in catalytic activity of F doped oxide thin film materials in comparison to the undoped oxide system is expected to occur as a result of improved surface reactivity occurring in conjunction with electronic structure modification (in addition to improvement in conductivity) [34]. The surface catalytic activity of the electro-catalyst can also be improved by the synthesis of high electrochemically-active surface area nanosized electro-catalyst powders expectedly resulting in reduced noble-metal catalyst loading to ultra-low levels and ease of coating the electro-catalyst layer on the proton exchange membrane for full cell fabrication.

Previous work into thin film electrocatalysts based on $(Nb_{0.80}Ir_{0.20})O_2:F$ showed improved catalytic activity in comparison to pure $(Nb_{0.75}Ir_{0.25})O_2$ and comparable electrochemical performance to pure IrO_2 [28] though Nb_2O_5 and $Nb_2O_5:F$ are electrochemically inactive as anodes for PEM electrolysis. However, with the addition of IrO_2 in minute amounts to Nb_2O_5 or the doped form of $Nb_2O_5:F$ a homogeneous solid solution of $Nb_2O_5/ Nb_2O_5:F$ and IrO_2 [denoted hereafter as $(Nb, Ir)O_2:F$] is formed exhibiting excellent catalytic activity for the oxygen evolution process. With this strategy in mind, a high active surface area nanostructured solid solution of Nb_2O_5 or $Nb_2O_5:F$ and IrO_2 in the bulk powder form (nominal composition: $(Nb_{1-$

$y\text{Ir}_y\text{O}_2$:x wt.% F ; $y \sim 10$ to 80; $x \sim 0$ and 10) [32, 35-39] has been synthesized by a two-step chemical synthesis process. These electro-catalysts were then made into an ink form using a binder coated onto a porous Ti foil for further testing as an anode for OER in PEM based water electrolysis. In the present study accordingly, we will present the electrochemical response for the catalyst consisting of a nanocrystalline Nb_2O_5 :F and IrO_2 solid solution with an optimal composition of $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$:x wt.% F; $x = 0$ and 10, displaying excellent electrochemical performance comparable to pure F doped IrO_2 . Various characterization techniques including x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), transmission electron microscopy (TEM) along with the structural stability test (chronoamperometry) of the $(\text{Nb},\text{Ir})\text{O}_2$:F electro-catalyst have been conducted to better understand structure-electrochemical activity relationships. In tandem with experimental catalyst evaluation, first principles calculations of the total energies, electronic structures and cohesive energies of the system were performed for validation of experimentally observed trends.

2. Experimental and Computational Details:

2.1 Electro-catalyst preparation:

High surface area Nb_2O_5 and Nb_2O_5 :F powders were synthesized using metal chloride precursor based sol-gel method previously reported by this group [40]. In short, Nb_2O_5 :F was prepared by dissolving NbCl_5 [99.95%, Alfa Aesar] powder in absolute ethanol (200 proof, Fisher Scientific) inside an atmosphere controlled glove box (MBraun Unilab Work station) and mixing suitable amount of fluorine precursor, trifluoroacetic acid [CF_3COOH , 99%, Alfa Aesar]

followed by hydrolysis using 0.3M ammonium hydroxide solution. The hydrolyzed product was washed with D.I. water multiple times and the white precipitate thus obtained was converted into a yellow sol by the addition of 6 wt.% hydrogen peroxide. This sol was then allowed to gel in a sealed round bottom flask at 75°C for 24 hours and subsequently dried at 75°C for 48 hours to form high specific surface area (SSA) Nb₂O₅:10F and pure Nb₂O₅ oxides, respectively. (Nb,Ir)O₂:10F powders were prepared by soaking suitable amount of IrCl₄ [99.95%, Alfa Aesar] ethanol solution on the surface of the as-prepared Nb₂O₅ or Nb₂O₅:F. The soaked powder was then dried at 60°C and heat treated in air at 673 K for 4 hours in order to form the (Nb,Ir)O₂ or (Nb, Ir)O₂:10F solid solution powders.

2.2 Physical and chemical Characterization:

The synthesized powder materials were analyzed by performing x-ray diffraction (XRD) on a Philips XPERT PRO system (with CuK_α radiation) in the 2θ range of 20° – 80°. The operating voltage and current were kept constant at 45 kV and 40 mA respectively. Crystallite size of the (Nb_{1-x}Ir_x)O₂:10F of different compositions was estimated by performing peak profile analysis using the single line approximation method and applying the Scherrer formula (after performing instrumental broadening corrections and lattice strain correction) [41]. The specific surface area of the electro-catalyst powders was measured by performing nitrogen adsorption-desorption studies (on a Micromeritics ASAP 2020) and analyzing the data using the Brunauer-Emmett-Teller (BET) isotherm. The powder was first vacuum degassed and then tested using multipoint BET analysis. Microstructural characteristics of these electro-catalysts were examined using SEM (Philips XL-30FEG) and TEM (on a JEOL 4000EX operating at 400 kV).

Quantitative elemental analysis and distribution of elements (x-ray mapping) was investigated using the energy dispersive x-ray spectroscopy (EDX) analyzer integrated into the SEM unit.

X-ray photoelectron spectroscopy (XPS) was performed on the catalysts in order to determine the oxidation states of the Ir, Nb and O present in the $(\text{Nb}_{1-x}\text{Ir}_x)\text{O}_2\cdot 10\text{F}$ system. The catalysts were analyzed by performing XPS on a Physical Electronics (PHI) model 32-096 X-ray source control with a 22-040 power supply interfaced to a model 04-548 x-ray source attached to an Omni Focus III spherical capacitance analyzer (SCA). The system was operated within the pressure range of 10^{-8} to 10^{-9} Torr with calibration performed utilizing the photoemission lines E_b of Cu $2p_{3/2}$ (932.7 eV), E_b of Au $4f_{7/2}$ (84 eV) and E_b of Ag $3d_{5/2}$ (368.3 eV) for a magnesium anode. Charge correction was obtained by referencing the adventitious C 1s peak to 284.8 eV and intensities are experimentally determined peak areas divided by the instrumental sensitivity factors.

2.3 Electrochemical Characterization:

$(\text{Nb}, \text{Ir})\text{O}_2\cdot 10\text{F}$ solid solution powder catalyst inks consisting of 85 wt.% catalyst and 15 wt.% Nafion solution [5 wt.% solution in lower aliphatic alcohols, Sigma Aldrich] were prepared by suitable homogenization. Working electrodes (1 cm^2) were prepared by spreading the catalyst inks (total loading of the $(\text{Nb}_{1-x}\text{Ir}_x)\text{O}_2\cdot 10\text{F}$ electro-catalyst on the Ti foil was maintained at $\sim 0.3\text{ mg/cm}^2$) uniformly on a 50% porous titanium foil (Accumet Materials Co.). Electrochemical testing was performed on a 3-electrode test system with a five port jacketed reaction cell (Ace Glass Inc.) maintained at 40°C (using a Fisher Scientific 3006S Isotemp Refrigerator Circulator) as described elsewhere [11, 32, 35, 38] with the catalyst samples used as the working electrode,

161 mercury/mercurous sulfate reference electrode [$\text{Hg}/\text{Hg}_2\text{SO}_4$, $\sim +0.65$ V with respect to the
162 standard hydrogen electrode (SHE/NHE)] (XR 200, Radiometer Analytical) and a Platinum foil
163 (Alfa Aesar, 0.25 mm thick, 99.95%) counter electrode. A solution of 1 Normal sulfuric acid (1N
164 H_2SO_4) was used as the electrolyte. The electrolyte was de-aerated with ultra-high purity (UHP)
165 argon gas for 30 minutes prior to conducting electrochemical tests. Potentiodynamic polarization
166 tests were performed on VersaSTAT-3 potentiostat (Princeton Applied Research) employing a
167 scan rate of 1 mV/s from 0 V to 2 V (*vs.* NHE). Reaction kinetics on the various (Nb, Ir) O_2 :10F
168 solid solution powder catalysts was compared using the Tafel slope (b) from the plot of the over-
169 potential (η) *vs.* log current[42-46].

170 Electrochemical impedance spectroscopy (EIS) was performed on the various (Nb,
171 Ir) O_2 :10F solid solution powder catalysts cast electrodes in the three-electrode setup described
172 above in the frequency range of 100 mHz – 100 kHz using VersaSTAT 3 (Princeton Applied
173 Research) at an amplitude of 10 mV. Nyquist impedance spectra were analyzed using ZView
174 software from Scribner Associates and was used to determine the solution resistance (R_s),
175 electrode resistance (R_e) and the polarization resistance (R_{ct}) of the electro-catalyst using the
176 circuit models of $R_s(R_e Q_1)(R_{ct} Q_{dl})$ reported earlier[32, 38]. Constant phase elements (CPE) were
177 used in place of capacitances as is commonly done in porous powder based electrode systems
178 wherein Q_1 , Q_{dl} are the CPEs associated with the electrode, double layer capacitance and
179 pseudocapacitance contributions[27, 42]. Ohmic resistance has been calculated using ($iR_s + iR_e$)
180 to compensate for the ohmic loss (iR_Ω) correction in the polarization curves. The polarization
181 resistance (R_{ct}) has been used to understand the electrochemical activity of the electro-catalyst.
182 Chronoamperometry (CA) was performed on the catalyst samples at a constant voltage of ~ 1.65
183 V (*vs.* NHE) for 12 hours using 1N H_2SO_4 as an electrolyte in the same three electrode cell

configuration to study long term structural stability. In tandem, inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP 6500 duo Thermo Fisher) was performed in order to study the elemental composition of the electrolyte (H_2SO_4), collected after CA testing, with the aim of determining the amount of iridium and niobium leached out into the solution from the electrode.

2.4 Computational methodology and details:

Ab-initio theoretical electronic structure and cohesive energy calculations were performed on the $(\text{Nb}_{1-x}\text{Ir}_x)\text{O}_2$ and $(\text{Nb}_{1-x}\text{Ir}_x)\text{O}_2:10\text{F}$ catalyst systems in order to qualitatively relate composition with catalytic activity, electronic conductivity, and long term stability respectively[28-33, 38]. In order to do this, representative compositions $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$ and $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_{1.25}\text{F}_{0.75}$ were chosen to obtain a deeper insight into the intrinsic properties of undoped as well as doped oxide with ~ 9.4 wt.% F corresponding to the formula unit $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_{1.25}\text{F}_{0.75}$ respectively. Calculations of the electronic structure, equilibrium lattice parameters and cohesive energies of the materials have been conducted using the density functional theory (DFT) methodology implemented in the Vienna Ab-initio Simulation Package (VASP)[47-49]. The projector augmented wave (PAW) method with the generalized gradient approximation (GGA) for the exchange-correlation energy functional[50] has been applied in present study.

In order to accurately determine the internal atomic positions and hence, the total energy of the system, the lattice parameters and internal positions of atoms were fully optimized employing the double relaxation procedure, where all atoms were allowed to relax (with the

residual force components on each atom to be lower than 0.01 eV/Å/atom). The Monkhorst-Pack scheme was used to sample the Brillouin Zone (BZ) and generate the k -point grid (k -points in the irreducible part of the BZ was based on convergence of the total energy ~ 0.1 meV/atom) for the solids and the different isolated atoms used in the present study. Standard PAW potentials were employed for the elemental constituents of all pure and doped compounds in the study.

As a model system, a 12-atom supercell containing two rutile type unit cells has been constructed to represent the two compositions of the materials considered in the theoretical section. The $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_{1.25}\text{F}_{0.75}$ composition could be represented by different spatial configurations with 5 atoms of O and 3 atoms of F distributed randomly over 8 available oxygen sites in the 12-atom super cell used for the calculations. In order to eliminate the uncertainty associated with the atomic distribution, several atomic configurations for this specific composition have been considered. A configuration corresponding to the minimal total energy has thus been selected for further analysis. For calculation of the (1 1 0) surface electronic properties of the materials a two-dimensional slab containing four oxygen and three metal layers repeated in (1 -1 0) direction with ~ 7 Å of thickness and a vacuum distance of ~ 14 Å between adjacent images of the slab was selected. The results of the studies conducted are described below.

3. Results and Discussion:

The specific surface area (SSA), measured by N_2 adsorption/desorption BET techniques, of the as-prepared Nb_2O_5 and $\text{Nb}_2\text{O}_5:10\text{F}$ powder synthesized by the sol gel method is ~ 257 m²/g and ~ 389 m²/g (Fig. S1), respectively. The XRD patterns of the optimized compositions

(Nb_{0.75}Ir_{0.25})O₂ and (Nb_{0.75}Ir_{0.25})O₂:10F electro-catalyst, shown in Fig. 1, synthesized after thermal treatment at ~673 K of a mixture of high surface area Nb₂O₅/Nb₂O₅:F and IrCl₄, shows all the peaks corresponding to single phase tetragonal structure (PDF number: 01-088-0288; ICSD: 84577)[51-55]. This result clearly suggests the formation of single phase tetragonal solid solution of Nb₂O₅/Nb₂O₅:F and IrO₂ indicated as, [(Nb,Ir)O₂:F], with no phase segregation (*e.g.* IrO₂+ Nb₂O₅) and/or two-phase formation. The calculated molar volume of the tetragonal (Nb_{0.75}Ir_{0.25})O₂:10F (19.7 cm³/mol of lattice parameter $a=4.582$ Å, $c=3.112$ Å) is lower than the theoretical molar volume of tetragonal NbO₂ (~21.17 cm³/mol) which reaffirms the incorporation of the lower volume IrO₂ (~19.22 cm³/mol) into the NbO₂ lattice to form the observed solid solution. It is therefore interesting to note that the presence of 25 at.% tetragonal IrO₂ solute into the lattice of the monoclinic Nb₂O₅ stabilizes the tetragonal structure of [(Nb,Ir)O₂:F]. Peak profile analysis of the obtained XRD pattern was performed using single line approximation method after eliminating the instrumental broadening and lattice strain contribution,[56] The effective particle size of (Nb_{0.75}Ir_{0.25})O₂ and (Nb_{0.75}Ir_{0.25})O₂:10F, calculated using the Scherrer formula from the integral breadth of the Lorentzian contribution was determined to be ~5 nm. This was also evidenced by bright field TEM image of (Nb_{0.75}Ir_{0.25})O₂:10F (Fig. S2-S3), wherein nanometer sized fine particles in the range of ~4-8 nm are distinctly observed. The BET specific surface area of the Ir containing solid solution of (Nb_{0.75}Ir_{0.25})O₂ and (Nb_{0.75}Ir_{0.25})O₂:10F, measured by multilayer adsorption-desorption isotherm, was found to be ~77 m²/g and ~99 m²/g, respectively.

Quantitative elemental composition analysis of the synthesized powders was performed on the (Nb_{0.75}Ir_{0.25})O₂:10F by performing EDX on the SEM machine. Fig. S4 shows the EDX

pattern of $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2\cdot 10\text{F}$ which confirms that the measured elemental compositions of Ir
 and Nb are close to the nominal composition as indicated in the table inset in Fig. S4
 (homogeneity of the elements is seen in Fig. S5). Figs. 2a, 2b and 2c depict the surface
 composition and chemical oxidation states (Ir-4f, Nb-3d and O-1s) of $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$ and
 $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2\cdot 10\text{F}$, respectively obtained by performing x-ray photoelectron spectroscopy
 (XPS) on the synthesized electro-catalysts. A distinct doublet with binding energies of ~ 61.6 eV
 and ~ 64.5 eV is observed in Fig. 2a corresponding to Ir $4f_{7/2}$ and Ir $4f_{5/2}$ peaks in $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$.
 Nb $3d_{5/2}$ and Nb $3d_{3/2}$ peaks with a binding energy of ~ 207.5 eV and ~ 210.3 eV, respectively
 corresponding to those of stoichiometric NbO_2 are seen in Fig. 2b. The position of O 1s peak at
 ~ 530.5 eV matches that of bulk IrO_2 . In the case of $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2\cdot 10\text{F}$ a shift in binding energy
 of Ir 4f, Nb 3d and O1s core level by $\sim 0.4 - 0.6$ V with respect to $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$ is observed in
 Figs. 2a, 2b and 2c. Unequivocal identification of fluorine from XRD, EDX, and XPS
 measurements is not possible[32, 57, 58]. However, the peak shift observed herein is an indirect
 indication of the presence of fluorine in the $(\text{Nb},\text{Ir})\text{O}_2$ lattice which is expected to result in
 stronger binding on account of its higher electro-negativity. The presence of fluorine in the
 lattice is additionally confirmed by the changes in electrochemical properties, occurring as a
 result of improved electronic structure, electronic conductivity and durability of the fluorine
 doped oxide solid solution, discussed in the following sections as well as reported by present
 authors in other publications[11, 28, 32, 35, 38, 39].

The synthesized tetragonal nanostructured $(\text{Nb},\text{Ir})\text{O}_2$ and $(\text{Nb},\text{Ir})\text{O}_2\cdot \text{F}$ has been examined
 as a promising OER anode electro-catalyst for PEM (proton exchange membrane) based water
 electrolysis. In the present article, the electrochemical performance of optimized compositions

276 $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$ and $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2\cdot 10\text{F}$ electro-catalyst has been presented. In addition, the
 277 electrochemical performance of commercially obtained high surface area hydrated IrO_2 (Alfa
 278 Aesar) and the in-house synthesized high surface area IrO_2 has been studied in order to compare
 279 the electrochemical performance of the tetragonal $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2\cdot 10\text{F}$ with pure $\text{IrO}_2/\text{IrO}_2\cdot \text{F}$. A
 280 detailed electrochemical study of the in-house synthesized high surface area nanostructured
 281 $\text{IrO}_2\cdot \text{F}$ powder has already been published by us and reported[28]. Therefore, the detailed study
 282 has not been presented in this article. It must be mentioned however herein, that hydrated IrO_2
 283 from Alfa Aesar is considered and accepted to be the best OER catalyst based on electrochemical
 284 activity though its long term stability/durability has been considered to be poor due to the
 285 presence of amorphous IrO_2 and metallic Ir (Fig. S6). Fig. 3 depicts the polarization curves of
 286 commercial hydrated IrO_2 (Alfa Aesar), $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$ and $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2\cdot 10\text{F}$, conducted in the
 287 presence of 1N H_2SO_4 solution at 40°C with a scan rate of 1 mV/sec. The plot depicts both as-
 288 obtained curves and iR -corrected curves wherein ohmic resistance (R_Ω) encountered as a result
 289 of a combination of solution resistance (R_s), electrode (R_e) and bubble resistance (R_{bub}) have
 290 been accounted for in order to reflect true electrocatalyst activities[44, 45]. The value of R_s , and
 291 R_e of different catalyst, obtained from EIS measurements conducted at different potentials which
 292 will be discussed in details later, is presented in Table 1. The polarization curves of commercial
 293 IrO_2 (Alfa Aesar), $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$ and $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2\cdot 10\text{F}$, after ohmic resistance correction (iR_Ω
 294 $= iR_s + iR_e$), are also plotted in Fig. 3. The water splitting reaction (OER) for commercial hydrated
 295 IrO_2 occurs at a potential of $\sim 1.43\text{V}$ vs. NHE (Fig. 3). The onset potential is defined as the
 296 potential value at which the tangents drawn to the rising curve in the activation polarization
 297 region (*i.e.* the kinetic regime) intersect each other. The current density of commercial hydrated
 298 IrO_2 and in house synthesized IrO_2 at $\sim 1.5\text{V}$ (vs. NHE) (a typical voltage selected to verify the

electrochemical activity for water electrolysis) obtained from iR_{Ω} corrected plot is $\sim 0.0125 \pm 0.0002 \text{ A/cm}^2$ and $\sim 0.013 \pm 0.0002 \text{ A/cm}^2$, respectively, for $\sim 0.3 \text{ mg/cm}^2$ total loading of the catalyst. The polarization curve for the $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$ and $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2:10\text{F}$ before and after iR_{Ω} correction (Fig. 3) also shows OER occurring at a potential of $\sim 1.43 \text{ V}$ (vs. NHE) which is identical to that of pure commercial IrO_2 and that of the published results of in-house synthesized high surface area IrO_2 [28]. However, the current density at $\sim 1.5 \text{ V}$ (vs. NHE) for $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$ with the identical total electro-catalyst loading of $\sim 0.3 \text{ mg/cm}^2$ is only $\sim 0.008 \pm 0.0002 \text{ A/cm}^2$ at 40°C which is $\sim 36\%$ lower than the commercial IrO_2 and the in house synthesized IrO_2 . It has also been identified that the current density of $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$ increases with increase in F doping and reaches an optimum value at 10wt.% F. An optimum composition, $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2:10\text{F}$ shows a current density of $\sim 0.0133 \pm 0.0002 \text{ A/cm}^2$ at $\sim 1.5 \text{ V}$ (vs. NHE) which is comparable to commercial IrO_2 (Fig. 3) and in house synthesized high surface area pure IrO_2 [28].

In order to understand the electrochemical reaction kinetics of $(\text{Nb}_{1-x}\text{Ir}_x)\text{O}_2:10\text{F}$ which depend on the polarization resistance, electrochemical impedance spectroscopy (EIS) was used to study the charge transfer/polarization resistance (R_{ct}) at the catalyst/electrolyte interface. The EIS study has also been used to obtain the ohmic resistance (R_{Ω}) of studied electro-catalysts. Figure 6a, 6b and 6c show the EIS plot of $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$, $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2:10\text{F}$ and commercial hydrated IrO_2 respectively, measured at open circuit potential (OCP), 1.5 V and 1.6 V in the frequency range of 100 mHz - 100 kHz . The experimentally obtained Nyquist plots are fitted to a circuit model described earlier $[R_s(R_eQ_1)(R_{\text{ct}}Q_{\text{dl}})]$ using ZView software from Scribner Associates in order to obtain fundamental electrochemical parameters (Table 1). Characteristic

semi-circular arcs (Fig. 4a, 4b and 4c) are observed in the Nyquist plots with an almost voltage-independent series resistance, R_s of $\sim 16.8 \Omega$ in the case of both the undoped and F doped electrocatalysts. The diameter of this arc is typically a measure of the charge transfer/polarization resistance (R_{ct}). As shown in Fig. 4 and Table 1, $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2:10\text{F}$ has similar or even lower polarization resistance (R_{ct}) values compared to commercial IrO_2 and in house synthesized IrO_2 as seen in Table 1. On the other hand, undoped $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$ exhibit higher R_{ct} values which decreases with the incorporation of F in the lattice. The decrease of polarization resistance with increase in F content explains the increase in catalytic activity of the electrode with incorporation of F. The Tafel plot, after accounting for the iR_Ω correction of commercial IrO_2 is shown in Fig. 5, which has a Tafel slope of $\sim 83 \text{ mV/decade}$, which is slightly higher than that corresponding to the two electron pathway reaction (Tafel slope $\sim 62 \text{ mV/dec}$) assuming the transfer coefficient to be ~ 0.5 [26, 27, 32, 38, 46]. The Tafel slope of $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$ and $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2:10\text{F}$, calculated from the corresponding iR_Ω corrected Tafel plots, shown in Fig. 5, is ~ 132 and $\sim 78 \text{ mV/decade}$, respectively (see Fig. S8-upon use of SSA to calculate the same, values are almost identical i.e. ~ 148 and $\sim 79 \text{ mV/decade}$). The decrease in Tafel slope with increasing F content suggests an increase in the number of electrons produced in OER with increase in F content. The activity reaches an optimal value for $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2:10\text{F}$ exhibiting very similar electro-catalytic activity to that of commercial IrO_2 ($\sim 83 \text{ mV/decade}$) and in-house synthesized IrO_2 ($\sim 93 \text{ mV/decade}$). The above results clearly show that $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2:10\text{F}$ is indeed a promising electro-catalyst for OER with 75 at.% reduction in noble metal IrO_2 loading due to its lower reaction polarization resistance reflected as an observed improvement in electrochemical reaction kinetics.

Chronoamperometry (CA) was performed on the undoped $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$, $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$:10 wt.% F and the commercial IrO_2 control catalyst samples over a period of 12 h at a potential of ~ 1.65 V (vs. NHE) to observe possible degradation or catalyst deactivation and are shown in Fig. 6. It can be observed that the commercial IrO_2 material has a rapid decay in capacity, possibly due to instability and rapid deactivation. The decay of current for $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$, $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$:10 wt.% F catalysts can be attributed to dissolution of coating at the edge of the porous titanium support[26], and by the induced loss of electrolyte[32, 35]. The doped $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$:10 wt.% F exhibits superior initial current density as expected as a result of superior electrocatalytic activity as observed in Fig. 3. No dissolution of Ir or Nb in 1N H_2SO_4 electrolyte solution was observed by performing ICP on the post-cycled electrolyte in the case of both the doped and undoped $(\text{Ir,Nb})\text{O}_2$ catalyst materials indicating that observed fade is possibly a result of deactivation and electrolyte loss. CA of in-house synthesized IrO_2 bears similar results and is explained in detail in the published article[28]. Thus, the formation of solid-solutions of Nb_2O_5 :F into IrO_2 significantly enhances electrochemical stability.

It can be seen that the performance of the $(\text{Ir}_{0.25}\text{Nb}_{0.75})\text{O}_2$, and $(\text{Ir}_{0.25}\text{Nb}_{0.75})\text{O}_2$:10 wt.% F catalysts are identical to those seen in Fig. 3 and Fig. 6 respectively when evaluated with respect to SSA (see Figs. S7 and S9). The current density at ~ 1.5 V (vs. NHE) for $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$ with the identical total electro-catalyst loading of ~ 0.3 mg/cm² is ~ 33.522 $\mu\text{A}/\text{cm}^2$ (SSA) at 40°C i.e. $\sim 25.5\%$ lower than the current density of $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$ at 10wt.% F (current density of ~ 45.018 $\mu\text{A}/\text{cm}^2$ at ~ 1.5 V (vs. NHE)). In addition, the gravimetric current density (A/g-Ir) (Fig. S10) is far superior for the $(\text{Nb}_{1-x}\text{Ir}_x)\text{O}_2$ and $(\text{Nb}_{1-x}\text{Ir}_x)\text{O}_2$:10F systems than the commercial IrO_2 material which is to be expected given the reduction in noble metal content with no concomitant

reduction in electrochemical activity. Similarly, in Fig. S9, it can be seen that $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$, 10wt.% F has superior stability than $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$.

Theoretical first principles studies were performed in tandem with the experimental electrochemical studies in order to understand and establish the possible reasons for improved electrocatalytic activity and long-term structural stability of fluorine doped $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$. Fig. 7 depicts the total densities of electronic states calculated for pure IrO_2 as well as for undoped and F doped $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$. The band structure of IrO_2 has been discussed elsewhere[39]. Introduction of Nb and F into the IrO_2 matrix changes the electronic structures of the compounds significantly as shown in Fig. 7 with all the materials remaining metallic with differing electronic conductivities. The density of states at the Fermi level $n(E_F)$ is a qualitative measure of electronic conductivity and Table 2 collects the values of $n(E_F)$ corresponding to all the three compositions discussed here. The $n(E_F)$ value for pure IrO_2 decreases drastically upon introduction of niobium oxide into IrO_2 resulting in a drop in the electronic conductivity which is to be expected since Nb_2O_5 is a wide band gap (~ 3.9 eV) insulator[59]. Doping with fluorine in $\text{Ir}_{0.25}\text{Nb}_{0.75}\text{O}_2$: 10 wt.% F however offsets the drop in density of states significantly improving the overall conductivity as indicated in Table 2 and possibly resulting in the much higher current density and electrocatalytic activity (observed before iR correction) in tandem with enhanced kinetics (see Fig. 5). A similar effect has previously been reported by this group[11, 36, 39] in the case of fluorine doped SnO_2 and IrO_2 - SnO_2 - Nb_2O_5 solid solutions with significant improvement in the electronic conductivity due to an increase in the charge carrier concentrations in the system.

A second part of the theoretical study is the evaluation of electrocatalytic activity of the various compositions in order to find an optimal position of ϵ_d (gravity center of the noble metal d-band) providing an optimal interaction between the various species adsorbed on the catalyst

surface in the elementary steps of the water electrolysis process as has been previously identified by Nørskov *et al.* [60, 61]. Using pure IrO₂ as the gold-standard OER catalyst, electronic structure calculations were performed on the stable and catalytically active (1 1 0) surface of the undoped and F-doped Ir_{0.25}Nb_{0.75}O₂ with the aim of defining the Ir d-band center position and qualitatively evaluating the electro-catalytic activity in comparison to IrO₂. The positions of the corresponding Ir d-band centers have been obtained as a first moment of $n_d(E)$: as follows:

$$\varepsilon_d = \int n_d(E)E dE / \int n_d(E) dE.$$

The reference point for the optimal position of the d-band i.e. pure IrO₂ is ~ -1.33 eV below the Fermi level as shown in Fig. 8a. Fig. 8 depicts the partial Ir d-band densities of states for the three compositions together with the corresponding ε_d centers (marked with vertical arrows). In the case of Ir_{0.25}Nb_{0.75}O₂ (Fig. 8b), partial Ir 5d - Nb 4d hybridization wherein the Nb 4d electronic states lie above Ir 5d states on the energy scale results in a noticeable shift of the Ir d-band center up towards the Fermi level ($\varepsilon_d \sim -0.95$ eV). This shift correlates very well with experimentally observed drop in catalytic activity seen in Ir_{0.25}Nb_{0.75}O₂ (Fig. 5). In Fig. 8c, it can be seen that in the presence of fluorine, ε_d moves back to a slightly lower position as compared to that of pure IrO₂. Fluorine 2p states are located below Ir 5d electrons and F 2p - Ir 5d hybridization results in the widening of Ir 5d band as compared to the corresponding states in undoped Ir_{0.25}Nb_{0.75}O₂. Thus, fluorine doping of Ir_{0.25}Nb_{0.75}O₂ leads to an improvement in the catalytic activity as compared to fluorine free Ir_{0.25}Nb_{0.75}O₂ composition also shown in Fig. 5. Table 2 shows the collected ε_d values calculated for all the three compositions and the similarity in electronic structure between IrO₂ and F doped (Ir,Nb)O₂, indicated by similar ε_d values is

probably a critical reason for the experimentally observed improvement in electro-catalytic activity of the F doped oxide.

Table 2 also depicts the theoretically calculated cohesive energy (E_{coh}) for the different compositions, a good indicator of chemical stability of the system. Stronger Nb-O bonds in comparison to Ir-O results in superior stability and durability (see Fig. 8) (evidenced by a more negative value in cohesive energy) of solid-solutions of Nb-IrO₂ oxide (calculated E_{coh} for pure NbO₂ is -18.251 eV/f.u. vs. -15.859 eV/f.u. for IrO₂). This effect however, is offset to an extent by further F doping into the Ir_{0.25}Nb_{0.75}O₂ mainly due to the lower ionic charge of F⁻ vs. O²⁻ which significantly weakens the electrostatic component of Ir-F and Nb-F bonds in comparison to those of Ir-O and Nb-O ionic bonds. It can be seen that this effect does not reflect in the chronoamperometry plots (Fig. 6) indicating the relative stability of Ir_{0.25}Nb_{0.75}O₂:F as compared to pure IrO₂. The above results therefore clearly indicate the promise of using Nb solid solutions of IrO₂ combined with F doping to generate F doped (Ir,Nb)O₂ nanoparticles as a potential catalyst system for PEM based water electrolysis.

4. Conclusion:

Nanostructured fluorine doped tetragonal (Nb,Ir)O₂ solid-solution electro-catalysts have been studied as a promising OER electro-catalyst for PEM based water electrolysis. Single phase tetragonal solid solution of F doped Nb₂O₅ and IrO₂ is observed in the XRD patterns for the synthesized electro-catalyst. The nanoparticulate catalysts show uniform distribution and no observed phase separation/segregation. The electrochemical performance measured *via* current

density, polarization resistance and Tafel slope is optimal for the composition of $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$: 10 wt.% F and is comparable to that of commercial hydrated IrO_2 and in-house synthesized IrO_2 . The stability of the $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2$: 10F electro-catalysts is also much better than commercial IrO_2 thus making it a viable candidate for use as an oxygen evolution reaction electro-catalyst in PEM based water electrolysis. Complementary theoretical study conducted has also demonstrated good correlation between the electronic structure peculiarities of the material and its excellent electro-catalytic properties are well confirmed by the comprehensive experimental observations. We thus conclude that the electro-catalyst $(\text{Nb},\text{Ir})\text{O}_2\text{:F}$ is potentially a preferred OER electro-catalyst for PEM water electrolysis resulting in ~75 at. % reduction in noble metal content. This would portend a significant reduction in the overall costs of PEM based electrolyzers with further possible optimizations of the materials morphologies contributing to further improvements in the kinetics of the ensuing pertinent electrochemical reactions.

Acknowledgment:

Research supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award DE-SC0001531. Financial support of the National Science Foundation, NSF-CBET 0933141 and NSF-CBET 1511390 is also gratefully acknowledged. PNK also acknowledges the Edward R. Weidlein Chair Professorship funds and the Center for Complex Engineered Multifunctional Materials (CCEMM) for procuring the electrochemical equipment and facilities used in this research work. The authors

also acknowledge the Pittsburgh Supercomputing Center (PSC) for allocation of the computational resources used for the study reported herein.

References:

- [1] K. Caldeira, A.K. Jain, M.I. Hoffert, *Science*, 299 (2003) 2052-2054.
- [2] M.F. Hordeski, Fairmont Press, 2009.
- [3] C.J. Winter, *Int. J. Hydrog. Energy*, 34 (2009) S1-S52.
- [4] L. Barreto, A. Makihiro, K. Riahi, *International Journal of Hydrogen Energy*, 28 (2003) 267-284.
- [5] G.W. Crabtree, M.S. Dresselhaus, M.V. Buchanan, *Physics Today*, 57 (2004) 39-44.
- [6] Q. He, T. Mugadza, X. Kang, X. Zhu, S. Chen, J. Kerr, T. Nyokong, *Journal of Power Sources*, 216 (2012) 67-75.
- [7] P. Millet, N. Mbemba, S.A. Grigoriev, V.N. Fateev, A. Aukauloo, C. Etievant, *International Journal of Hydrogen Energy*, 36 (2011) 4134-4142.
- [8] K. Zeng, D.K. Zhang, *Prog. Energy Combust. Sci.*, 36 (2010) 307-326.
- [9] Y.H.P. Zhang, W.-D. Huang, *Trends in Biotechnology*, 30 (2012) 301-306.
- [10] C.P. Depauli, S. Trasatti, *J. Electroanal. Chem.*, 396 (1995) 161-168.
- [11] K. Kadakia, M.K. Datta, O.I. Velikokhatnyi, P. Jampani, S.K. Park, P. Saha, J.A. Poston, A. Manivannan, P.N. Kumta, *Int. J. Hydrog. Energy*, 37 (2012) 3001-3013.
- [12] A. Marshall, B. Borresen, G. Hagen, M. Tsyppkin, R. Tunold, *Electrochim. Acta*, 51 (2006) 3161-3167.
- [13] A.V. Nikiforov, A.L.T. Garcia, I.M. Petrushina, E. Christensen, N.J. Bjerrum, *Int. J. Hydrog. Energy*, 36 (2011) 5797-5805.
- [14] K.M. Papazisi, A. Siokou, S. Balomenou, D. Tsiplakides, *Int. J. Hydrog. Energy*, 37 (2012) 16642-16648.
- [15] F.M. Sapountzi, S.C. Divane, E.I. Papaioannou, S. Souentie, C.G. Vayenas, *J. Electroanal. Chem.*, 662 (2011) 116-122.
- [16] S.D. Song, H.M. Zhang, X.P. Ma, Z.G. Shao, R.T. Baker, B.L. Yi, *Int. J. Hydrog. Energy*, 33 (2008) 4955-4961.
- [17] Y. Takasu, N. Yoshinaga, W. Sugimoto, *Electrochem. Commun.*, 10 (2008) 668-672.
- [18] Q. Wang, F. Wu, N. Wang, L. Wang, X. Zhang, *Electrochim. Acta*, 74 (2012) 227-234.
- [19] X. Wu, K. Scott, *Int. J. Hydrog. Energy*, 36 (2011) 5806-5810.
- [20] O.I. Velikokhatnyi, P.N. Kumta, *Physica B: Condensed Matter*, 404 (2009) 1737-1745.
- [21] G.Y. Chen, C.C. Waraksa, H.G. Cho, D.D. Macdonald, T.E. Mallouk, *J. Electrochem. Soc.*, 150 (2003) E423-E428.
- [22] A.T. Marshall, S. Sunde, M. Tsyppkin, R. Tunold, *International Journal of Hydrogen Energy*, 32 (2007) 2320-2324.
- [23] M. Morimitsu, R. Otagawa, M. Matsunaga, *Electrochim. Acta*, 46 (2000) 401-406.
- [24] G.P. Vercesi, J.Y. Salamin, C. Comninellis, *Electrochim. Acta*, 36 (1991) 991-998.
- [25] S. Ardizzzone, C.L. Bianchi, G. Cappelletti, M. Ionita, A. Minguzzi, S. Rondinini, A. Vertova, *J. Electroanal. Chem.*, 589 (2006) 160-166.
- [26] J.M. Hu, H.M. Meng, J.Q. Zhang, C.N. Cao, *Corrosion Science*, 44 (2002) 1655-1668.
- [27] E. Rasten, G. Hagen, R. Tunold, *Electrochimica Acta*, 48 (2003) 3945-3952.

497 [28] K.S. Kadakia, P.H. Jampani, O.I. Velikokhatnyi, M.K. Datta, S.K. Park, D.H. Hong, S.J. Chung, P.N.
498 Kumta, *Journal of Power Sources*, 269 (2014) 855-865.

499 [29] K. Kadakia, M.K. Datta, O.I. Velikokhatnyi, P.H. Jampani, P.N. Kumta, *International Journal of*
500 *Hydrogen Energy*, 39 (2014) 664-674.

501 [30] K. Kadakia, M.K. Datta, O.I. Velikokhatnyi, P. Jampani, S.K. Park, S.J. Chung, P.N. Kumta, *Journal of*
502 *Power Sources*, 245 (2014) 362-370.

503 [31] K. Kadakia, M.K. Datta, P.H. Jampani, S.K. Park, P.N. Kumta, *Journal of Power Sources*, 222 (2013)
504 313-317.

505 [32] M.K. Datta, K. Kadakia, O.I. Velikokhatnyi, P.H. Jampani, S.J. Chung, J.A. Poston, A. Manivannan, P.N.
506 Kumta, *Journal of Materials Chemistry A*, 1 (2013) 4026-4037.

507 [33] K. Kadakia, M.K. Datta, O.I. Velikokhatnyi, P. Jampani, S.K. Park, P. Saha, J.A. Poston, A. Manivannan,
508 P.N. Kumta, *international journal of hydrogen energy*, 37 (2012) 3001-3013.

509 [34] O.I. Velikokhatnyi, K. Kadakia, M.K. Datta, P.N. Kumta, *The Journal of Physical Chemistry C*, 117
510 (2013) 20542-20547.

511 [35] K. Kadakia, M.K. Datta, P.H. Jampani, S.K. Park, P.N. Kumta, *Journal of Power Sources*, 222 (2013)
512 313-317.

513 [36] O.I. Velikokhatnyi, P.N. Kumta, *Physica B: Condensed Matter*, 406 (2011) 471-477.

514 [37] O.I. Velikokhatnyi, P.N. Kumta, *Journal of Power Sources*, 202 (2012) 190-199.

515 [38] K. Kadakia, M.K. Datta, O.I. Velikokhatnyi, P. Jampani, S.K. Park, S.J. Chung, P.N. Kumta, *Journal of*
516 *Power Sources*, 245 (2014) 362-370.

517 [39] K. Kadakia, M.K. Datta, O.I. Velikokhatnyi, P.H. Jampani, P.N. Kumta, *International Journal of*
518 *Hydrogen Energy*, 39 (2014) 664-674.

519 [40] N. Uekawa, T. Kudo, F. Mori, Y.J. Wu, K. Kakegawa, *Journal of Colloid and Interface Science*, 264
520 (2003) 378-384.

521 [41] T.H. de Keijser, J.I. Langford, E.J. Mittemeijer, A.B.P. Vogels, *Journal of Applied Crystallography*, 15
522 (1982) 308-314.

523 [42] J. Cheng, H. Zhang, G. Chen, Y. Zhang, *Electrochim. Acta*, 54 (2009) 6250-6256.

524 [43] J.-M. Hu, J.-Q. Zhang, C.-N. Cao, *Int. J. Hydrog. Energy*, 29 (2004) 791-797.

525 [44] N. Krstajic, S. Trasatti, *Journal of Applied Electrochemistry*, 28 (1998) 1291-1297.

526 [45] A. Minguzzi, F.-R.F. Fan, A. Vertova, S. Rondinini, A.J. Bard, *Chemical Science*, 3 (2012) 217-229.

527 [46] J. Rossmeisl, Z.W. Qu, H. Zhu, G.J. Kroes, J.K. Norskov, *J. Electroanal. Chem.*, 607 (2007) 83-89.

528 [47] G. Kresse, J. Furthmüller, *Physical Review B*, 54 (1996) 11169-11186.

529 [48] G. Kresse, J. Furthmüller, *Computational Materials Science*, 6 (1996) 15-50.

530 [49] G. Kresse, D. Joubert, *Physical Review B*, 59 (1999) 1758-1775.

531 [50] J.P. Perdew, W. Yue, *Physical Review B*, 33 (1986) 8800-8802.

532 [51] A.A.F. Grupioni, E. Arashiro, T.A.F. Lassali, *Electrochimica acta*, 48 (2002) 407-418.

533 [52] K. Kadakia, M.K. Datta, O.I. Velikokhatnyi, P. Jampani, S.K. Park, P. Saha, J.A. Poston, A. Manivannan,
534 P.N. Kumta, *International Journal of Hydrogen Energy*, 37 (2012) 3001-3013.

535 [53] K. Kadakia, M.K. Datta, O.I. Velikokhatnyi, P.H. Jampani, P.N. Kumta, *International Journal of*
536 *Hydrogen Energy*, 39 (2014) 664-674.

537 [54] K.S. Kadakia, P. Jampani, O.I. Velikokhatnyi, M.K. Datta, S.J. Chung, J.A. Poston, A. Manivannan, P.N.
538 Kumta, *Journal of The Electrochemical Society*, 161 (2014) F868-F875.

539 [55] K.S. Kadakia, P.H. Jampani, O.I. Velikokhatnyi, M.K. Datta, S.K. Park, D.H. Hong, S.J. Chung, P.N.
540 Kumta, *Journal of Power Sources*, 269 (2014) 855-865.

541 [56] T.H. Dekeijser, J.I. Langford, E.J. Mittemeijer, A.B.P. Vogels, *J. Appl. Crystallogr.*, 15 (1982) 308-314.

542 [57] F.M. Amanullah, K.J. Pratap, V. Hari Babu, *Materials Science and Engineering: B*, 52 (1998) 93-98.

[58] A.A. Shaltout, H.H. Afify, S.A. Ali, Journal of Electron Spectroscopy and Related Phenomena, 185 (2012) 140-145.

[59] N.D. Landolt-Bornstein, Group, 3 (1982) 12.

[60] T. Bligaard, J.K. Nørskov, Electrochim. Acta, 52 (2007) 5512-5516.

[61] B. Hammer, J.K. Nørskov, Theoretical surface science and catalysis—calculations and concepts, in: H.K. Bruce C. Gates (Ed.) Advances in Catalysis, Academic Press, 2000, pp. 71-129.

Table 1: Impedance parameters obtained by fitting the experimental EIS data to the equivalent circuit $R_s(R_eC_1)(R_{ct}Q_{ct})$.

Voltage	Electro-catalyst	$R_s (\Omega\text{cm}^2)$	$R_e (\Omega\text{cm}^2)$	$R_{ct} (\Omega\text{cm}^2)$
Open Circuit	(Ir,Nb)O ₂ :0F	16.9	3.1	2958
	(Ir,Nb)O ₂ :10F	16.9	2.7	2445
	In-house IrO ₂	16.0	2.0	203.4
	IrO ₂ (Alfa)	16.4	4.0	3577
1.5V	(Ir,Nb)O ₂ :0F	16.7	6.1	77.6
	(Ir,Nb)O ₂ :10F	16.7	5.0	47.2
	In-house IrO ₂	16.0	3.2	36.4
	IrO ₂ (Alfa)	16.3	3.4	44.9
1.6V	(Ir,Nb)O ₂ :0F	16.7	4.7	17.9
	(Ir,Nb)O ₂ :10F	16.8	4.0	10.4
	In-house IrO ₂	16.0	2.1	11.5
	IrO ₂ (Alfa)	16.4	2.6	14.8

Table 2: Calculated values of density of electronic states at Fermi level $n(E_F)$, positions of the Ir-d band center ϵ_d , and the cohesive energy $-E_{coh}$ for the catalysts.

	$n(E_F)$ [el./eV/f.un.]	ϵ_d (eV)	$-E_{coh}$ [eV/f.un.]
IrO ₂	2.15	-1.33	15.86
Ir _{0.25} Nb _{0.75} O ₂	0.76	-0.95	20.20
Ir _{0.25} Nb _{0.75} O _{1.25} F _{0.75}	1.62	-1.41	18.81

Figures and Captions:

Figure 1: XRD pattern of undoped and doped $(\text{Nb}, \text{Ir})\text{O}_2:\text{F}$.

(Figure 2a)

(Figure 2b)

(Figure 2c)

Figure 2: The XPS spectra of Ir $4f_{7/2}$ and $4f_{5/2}$ doublet (a), Nb $3d_{5/2}$ and Nb $3d_{3/2}$ doublet (b) and O 1s (c) of $(\text{Nb},\text{Ir})\text{O}_2$ and $(\text{Nb},\text{Ir})\text{O}_2\cdot\text{F}$.

Figure 3: The polarization curve of undoped and doped (Nb,Ir)O₂:F along with commercial IrO₂ conducted in the presence of 1N H₂SO₄ solution at 40°C with a scan rate of 1mV/sec before and after iR_Ω correction.

(Figure 4a)

(Figure 4b)

(Figure 4c)

Figure 4: EIS spectra of (Nb,Ir)O₂ (a), (Nb,Ir)O₂:10 wt.% F (b), and commercial IrO₂ (c) obtained at open circuit potential (OCP), 1.5V and 1.6V performed in 1N H₂SO₄ at 40°C.

Figure 5: The Tafel plot of commercial IrO_2 , $(Ir_{0.25}Nb_{0.75})O_2$, and $(Ir_{0.25}Nb_{0.75})O_2:10 \text{ wt.\% F}$, after iR correction.

Figure 6: The variation of current vs. time in the chronoamperometry test of undoped and doped $(\text{Ir},\text{Nb})\text{O}_2:\text{F}$ performed in a 1N H_2SO_4 solution under a constant potential of $\sim 1.65\text{V}$ at 40°C .

Figure 7: Total density of states for IrO₂, (Ir_{0.25}Nb_{0.75})O₂, and (Ir_{0.25}Nb_{0.75})O_{1.25}F_{0.75}.

620

621 **Figure 8:** (1 1 0) surface Ir d-band projected DOS for IrO_2 (a), $(\text{Ir}_{0.25}\text{Nb}_{0.75})\text{O}_2$ (b), and

622 $(\text{Ir}_{0.25}\text{Nb}_{0.75})\text{O}_{1.25}\text{F}_{0.75}$ (c). The arrows denote positions of d-band centers ϵ_d .

Graphical Abstract

High surface area ($\sim 300\text{m}^2/\text{g}$) nanostructured powders of nominal composition $(\text{Nb}_{1-x}\text{Ir}_x)\text{O}_2$ and $(\text{Nb}_{1-x}\text{Ir}_x)\text{O}_2\cdot 10\text{F}$ have been synthesized and tested as oxygen evolution electro-catalysts for PEM based water electrolysis using a simple two-step chemical synthesis procedure. Superior electrochemical activity was demonstrated by fluorine doped compositions of $(\text{Nb}_{1-x}\text{Ir}_x)\text{O}_2$ with an optimal composition $(\text{Nb}_{0.75}\text{Ir}_{0.25})\text{O}_2\cdot 10\text{F}$ ($x=0.25$) demonstrating on-par performance with commercial hydrated IrO_2 and nanostructured in-house chemically synthesized IrO_2 . Using first principles calculations, the electronic structure modification resulting in $\sim 75\text{at.}\%$ reduction (experimentally observed) in noble metal content without loss in catalytic performance and stability has been established.