High throughput discovery of enhanced visible photoactivity in Fe–Cr vanadate solar fuels photoanodes

Lan Zhou, Dan Guevarra and John M Gregoire

Division of Engineering and Applied Science and Liquid Sunlight Alliance, California Institute of Technology, Pasadena, CA 91125, United States of America

* Author to whom any correspondence should be addressed.

E-mail: gregoire@caltech.edu

Keywords: high-throughput discovery, photoactivity, metal oxide, combinatorial materials science, solar fuels, photoanode

Abstract

Metal oxide solar absorbers are well suited for photoelectrochemical applications where requisite properties include stability in highly oxidizing environments, in addition to solar energy conversion. Metal vanadates are of particular interest due to their relatively low band gap energies compared to traditional, wide-gap photocatalysts. Concerted efforts on BiVO$_4$-based photoanodes have revealed multiple avenues for improving the solar conversion efficiencies for photon energies above 2.5 eV but have not addressed the ultimate performance limitations from the undesirably high band gap energy. Fe and Cr vanadates have a lower band gap and thus a higher potential solar conversion efficiency, although to-date the absorbed 2–2.5 eV photons are not effectively converted to the desired anodic photocurrent. By using combinatorial synthesis and high throughput screening, we demonstrate that cation substitutions with the monoclinic MVO$_4$ phase (M = Cr, Fe) improves the utilization of photons in this energy range. Given the portfolio of photoanode improvement techniques available, we suggest optimization of (Cr$_{0.5}$Fe$_{0.5}$)VO$_4$-based photoanodes as a promising path for enable solar fuel technologies.

1. Introduction

Using solar energy for renewable generation of fuels requires a photoelectrocatalyst that efficiently utilizes the solar resource to power the oxygen evolution reaction, which liberates protons and electrons from water for use in fuel-forming reactions [1–3]. Metal vanadates have been the most intensely studied family of visible-gap metal oxide photoanodes, with the monoclinic BiVO$_4$ being the center of attention over the past decade [4–8]. While BiVO$_4$ has served as an exemplar material for advancing our understanding of complex photoanodes and establishing mechanisms to improve photoanode performance, utilization of solar energy is intrinsically limited by the \( \geq 2.4 \) eV band gap, motivating transfer of the lessons learned with BiVO$_4$-based photoanodes to other metal vanadates with a lower band gap energy [9–11]. Perhaps the most valuable materials design tool emerging from the BiVO$_4$ work is the ability to dramatically improve conductivity and more generally carrier transport with substitutions on the cation sublattice. Among the dozens of metal vanadates with photoactivity below 2.4 eV, the most prominent systems are the Fe- and Cr-based vanadates wherein photoactive phases with band gaps below 2.4 eV include CrVO$_4$-orth, CrVO$_4$-mon, and Cr$_2$V$_4$O$_{13}$ [12] as well as Fe$_2$O$_3$, Fe$_2$VO$_4$ [13], Fe$_2$V$_4$O$_{13}$ [14], Fe$_3$O$_6$ [15], and FeVO$_4$-tri [16–26]. Of these, FeVO$_4$ with band gap in the range 2.0–2.3 eV has received the most attention and is identified as a locally optimal composition via combinatorial exploration of the Fe–V oxide system [16, 21]. Akin to \( \alpha $Fe$_2$O$_3$, photoelectrochemical (PEC) performance of triclinic FeVO$_4$ is limited by its low carrier mobility and short hole diffusion length [22]. Initial work on heterojunction and coated FeVO$_4$ provide routes for photoelectrode optimization [25, 26], which will be most effective upon optimization of the carrier transport and more generally the photoactivity of the FeVO$_4$-based photoanodes.
The cation-substitution strategy for improving the photoactivity of FeVO₄ was initially demonstrated via doping with W [18] or Mo [22] and was more explored using combinatorial synthesis and screening methods by Nguyen et al [27]. Cation substituents explored in that work include Zn, Ni, Cr, Mo, and W with cation concentrations up to 10%. The best photoactivity in phosphate-buffered, near-neutral pH electrolyte with broadband illumination was observed with 7% Cr. Cr substitutions into FeVO₄ as well as the converse Fe substitutions into CrVO₄ have been shown to exhibit composition-tuned band edge positions [28]. The complex composition dependence on electronic structure is emblematic of the broader family of M⁺³VO₄ orthovanadates [29], which exhibit complex composition-dependent crystal structure, cation ordering, and magnetic ordering with different transition metals and mixtures thereof on the M⁺³ sublattice [30–33]. Mixed phase iron bismuth vanadate compound has been demonstrated to maintain good mobility of BiVO₄ while extending visible light absorption by mixing FeVO₄ with BiVO₄ [22, 34]. Unlike M = (Bi, Fe), complete miscibility on the M⁺³ sublattice has been observed for M = (Cr, Fe), with cation ordering at the 1:1 composition resulting in the quaternary oxide CrFe(VO)₄ [35]. Similar miscibility has been observed in the M₂VₓO₁₃ system [36], motivating our exploration of Cr–Fe–V oxide photoanodes with substantial amounts of both Cr and Fe, as opposed to the more dilute-substitutions that were explored previously [27]. Since the path for outperforming BiVO₄-based materials commences with establishing substantial photoactivity between 2 and 2.4 eV, we investigate the spectrally-resolved compositional variation in photoactivity, demonstrating that compositions near (Cr₀.₅Fe₀.₅)VO₄ are optimal for photoactivity at both 2.1 and 2.4 eV, motivating future study of these quaternary oxides to efficiently utilize the solar resource and advance solar fuels technologies.

2. Method

2.1. Composition library synthesis

The continuous composition spread of Cr–Fe–V was synthesized by reactive co-sputtering in a custom-designed combinatorial sputtering system [37] at room temperature and followed by post-position anneal in air at 650 °C for 1 h. The library was deposited in a mixed atmosphere of O₂ (0.6 mTorr) and Ar (5.4 mTorr) using Cr, Fe, and V sources placed 120° apart with respect to the substrate plane of the 100 mm-diameter Pyrex glass with a conductive SnO₂:F (FTO) coating, which served as the electrical back contact to the thin film photoanodes. The deposition proceeded for 10 h with the radio-frequency (RF) powers on Cr, Fe, and V sources set to 42, 62, and 150 W, respectively, to obtain the desired composition spread. Characterization data for this composition library have been aggregated in [38].

2.2. Composition and structure characterization

The bulk metal compositions were characterized by x-ray fluorescence (XRF) measurements using an EDAX Orbis Micro-XRF system with an x-ray beam approximately 2 mm in diameter. The Cr K, Fe K, and V K XRF peak intensities were extracted from the Orbis software and converted to normalized compositions using the sensitivity factor for each element calibrated by commercial XRF calibration standards (MicromatterTM). The bulk crystal structure and phase distribution of composition library was determined by x-ray diffraction (XRD) measurements. XRD was acquired using a custom high throughput setup [39] incorporated into the bending-magnet beamline 1–5 of the Stanford Synchrotron Radiation Light Source at SLAC National Accelerator Laboratory. The characterization employed a monochromated 12.7 keV source in reflection scattering geometry with a 2D image detector. Diffraction images were processed into one-dimensional XRD patterns using WxDiff software with calibration from a LaB₆ powder standard, and further analyzed in the Bruker eva software.

2.3. Optical characterization

Optical properties of composition library were characterized using a custom-built, on-the-fly high-throughput scanning spectroscopy instrument [40]. The dual-sphere spectrometer recorded both transmittance (T) and reflectance (R) simultaneously at each sample, which were used to calculate the spectral absorption coefficient (α) up to a factor of film thickness (τ): \( \alpha \tau = \ln[(1 - R)/T] \). The molar absorption coefficient was calculated by making τ the molar thickness from the XRF-measured molar concentration of Cr, Fe, and V. For select compositions, the traditional thickness-normalized absorption coefficient was calculated by adjusting the molar absorption coefficient by the molar density of the phase identified by XRD.

2.4. Scanning droplet cell (SDC) photoelectrochemistry (PEC) measurements

PEC characterization was carried out in a custom-designed fiber-coupled front-side illumination SDC instrumentation with a Gamry G 300 potentiostat controlled by custom automation software [41]. PEC photoanode screening protocol on the pseudo-ternary composition spread were reported previously [42].
Measurements were performed in an aqueous 1 atm O$_2$-saturated borate electrolyte (pH 9) with 0.01 M sodium sulfite as sacrificial hole acceptor to increase the hole transfer kinetics at the film/electrolyte interface. A grid of 218 compositions was characterized with sequential chronoamperometries (CAS) under a series of light emitting diode (LED) illumination sources (3.2, 2.7, 2.4, and 2.1 eV) from which photocurrent and thus the spectral external quantum efficiency (EQE, also called incident photon-to-current efficiency) is calculated, as well as a toggled-illumination cyclic voltammetry (CV) under 3.2 eV illumination. At each sample, CAS were measured at 1.23 V versus reversible hydrogen electrode (RHE) with LEDs toggled with 0.5 s on/off illumination: 3.2 eV for 15 s, and 2.7, 2.4, and 2.1 eV all for 4 s each, and following CV from 1.23 V to 0.73 V and back to 1.53 V vs RHE (rate of 0.02 V s$^{-1}$) under 3.2 eV illumination with light toggling 2 s on and 1 s off.

2.5. Composition interpolation

The XRF and optical measurements were performed on the same set of 1521 samples across the library on a 2 mm grid. The XRD and PEC measurements were carried out on a coarser grid of 302 and 218 samples, respectively, and those sample compositions were calculated using linear interpolation in the Cartesian library position space.

2.6. X-ray photoelectron spectroscopy (XPS)

The near-surface composition of select samples was measured by XPS using a Krato Axis Ultra Nova spectrometer with a base pressure $<10^{-9}$ Torr. The x-ray source is a monochromatic Al K$_\alpha$ source at 1486.6 eV and operated at 150 W. The binding energy was calibrated to the C 1s peak position at 285 eV.

Elemental quantification was performed in the CasaXPS software using a Shirley background fitting of the Cr 2p, Fe 2p, and V 2p$_{3/2}$, and O 1s peaks in the survey scans with relative sensitivity factors of 2.427, 2.957, 1.411, and 0.711, respectively.

3. Results

3.1. Phase behavior of Cr–Fe–V oxide system

The utilization of combinatorial magnetron sputtering to explore (photo)electrocatalysts for solar fuel applications has greatly accelerated the materials discovery and development, especially for discovering cation off-stoichiometry compounds and complex mixed phase metal oxides [12, 43, 44]. To explore photoactivity of Cr–Fe–V oxides, the pseudo-ternary composition spread was prepared by reactive co-sputtering targeted at center composition of Cr:Fe:V = 1:1:2 followed by annealing at 650 °C in air. The non-confocal geometry of sputtering sources provided a continuous composition gradient spanning a 60–70 at.% range in the concentration of each cation element across the 100 mm-diameter FTO glass substrate. While oxygen is incorporated into the film during deposition, the oxygen stoichiometry of the photoanode samples is expected to be governed by the crystallization into metal oxide phases during the 650 °C anneal. For composition-based analyses, each photoanode sample is represented by its cation compositions measured by XRF.

Since the crystal structure of photoanode materials has a strong impact on the optical and PEC performance, a collection of 302 XRD patterns was used to identify the crystalline structure and distribution of each phase in the Cr–Fe–V pseudo-ternary composition spread. Unlike Bi–Cu–V oxide’s complex phase diagram (containing 13 different crystal phases in 19 unique combinations), which requires employing deep reasoning networks to solve the underlying phase behavior [45], the phase behavior of the Cr–Fe–V oxide system is relatively simple due to the miscibility of Cr and Fe in metal vanadates [35, 36]. The XRD patterns were analyzed by matching entries in the ICDD database, resulting in the identification of five primary phase structures summarized in table S1. Manual visualization of the XRD patterns revealed substantial peak shifting indicating the significant alloying or solid solution between Fe and Cr in a wide composition range. Thus the continuous solid solution phases are labeled as M$_2$V$_4$O$_{11}$, MVO$_3$-mon, and M$_2$O$_3$, where M = (Cr, Fe). Figure 1 shows the composition plots of each identified crystal phase with representative XRD patterns compared to ICDD library entries (see figure S1 for an alternate visualization) and resulting unique nine combinations of phase field labeled from A to I. The majority phase in the Cr–Fe–V oxide system is the monoclinic MVO$_3$, which exists in 86% of measured samples across V concentration of 0.2–0.7 and Fe, Cr concentration of 0.1–0.7 (seven out of nine phase fields). The 100% pure phase appears in the narrow V composition region of 0.5–0.54 (phase field E). In the neighboring phase field at lower and higher V concentration, the monoclinic MVO$_3$ phase is mixed with M$_2$O$_3$ (phase field F–H) and M$_2$V$_4$O$_{13}$ (phase field B–C), respectively. At very small V concentration below 0.3, M$_2$O$_3$ becomes the majority phase, and mixes with both CrVO$_4$-mon and CrVO$_4$-orth phases at Cr-rich side (Cr > 0.55, phase field G), while mixing with FeVO$_4$-tri at Fe-rich side (Fe > 0.6, phase field I).
Figure 1. Phase mapping in the Cr–Fe–V oxide system. (a) The map of each identified crystalline phase (numbered 1–5) is shown as a composition plot and (b) the color-coded phase map of unique nine combinations with phase field labeled on the top left. Two red arrows indicate selected two composition lines with V concentration of 0.54 and 0.24, respectively, where a series of XRD patterns show substantial peak shifting due to alloying. Phases where isostructural Cr- and Fe-based phases are known and labeled using $M = \text{Cr, Fe}$.

Figure 2. (Cr,Fe)VO$_4$ solid solution. The series of XRD patterns arranged according to the Fe/Cr ratio at V concentration of $0.54 \pm 0.01$ (indicated with red arrow in figure 1(b)). For the indicated 2-theta range, the XRD heat map visualizes the peak shifting as a function of Cr–Fe composition in the MVO$_4$-mon phase with the positions of select Miller indices shown with red labels. The peaks from the FTO underlayer are indicated by the $\ast$ symbol.

To illustrate the continuous solid solution in the Cr–Fe–V oxide system across a wide range of compositions, we selected samples with V concentration of 0.54 and 0.24, respectively, to visualize in figures 2 and S2. At V concentration around 0.54 (phase field E) in figure 2(a), all samples exhibit monoclinic MVO$_4$ structure with Fe/Cr ranging from 0.28 to 5.1, coinciding with an increasing unit cell volume (decreasing 2-theta values) and a decreasing monoclinic distortion (decreases in the difference between, e.g. the 330 and 003 peaks). The systematic shifting of peak positions to higher d-spacing (lower 2-theta) with increasing Fe concentration also occurs in the neighboring phase fields: M$_2$V$_4$O$_{13}$ at higher V concentration (phase field A), and M$_2$O$_3$ at lower V concentration (phase field F). Figure S2 illustrates the phase behavior at V concentration of 0.24, where MVO$_4$-mon and M$_2$O$_3$ are mixed with CrVO$_4$-orth at Cr-rich side and with FeVO$_4$-tri at Fe-rich side (across phase field G to F to I).
3.2. PEC characterization of Cr–Fe–V oxide system
Spectral EQE calculated using the photocurrent from CAs and incident LED light power was used to investigate the relationship between the PEC activity and the incident photon energy. The EQE at 1.23 V vs RHE for each of the four photon energies mapped in both library position space and composition space is shown in figure 3. While almost all Cr–Fe–V oxide compositions exhibited photoactivity under 3.2, 2.7, and 2.4 eV illumination, with decreasing photon energy the local EQE maximum moves from Fe-rich compositions at the edge of the composition library toward the center of the composition space. With 2.4 eV and 2.1 eV illumination, the top several performers all reside in phase field E from figure 1(b) where the monoclinic MVO$_4$ structure is the only phase observed by XRD. The global maximum in EQE at these photon energies is near Cr$_{0.23}$Fe$_{0.24}$V$_{0.53}$, and the toggled-illumination CA and CV data for this sample are shown in figure S3. The XRF-derived ratio of V/M in the optimal MVO$_4$ samples is approximately 1.13, whose difference from the formula unit value of 1.0 is comparable to the uncertainty of the XRF measurement. The optimal films may indeed be V-rich, which is analogous to similar V excess in BiVO$_4$ resulting in high-performance, phase-pure photoanodes \[46\].

3.3. Optical property of Cr–Fe–V oxide system
Optical characterization of the Cr–Fe–V oxide composition library proceed with characterization of the composition-dependence of the spectral absorption coefficient, $\alpha$. For each composition, absorption coefficient spectrum was obtained from measured transmittance ($T$) and reflectance ($R$), then molar absorption coefficients were averaged over three different ranges of incident photon energy and normalized with XRF-determined molar concentration of metals. Figure 4 shows the composition mapping of averaged molar absorption coefficients of 1521 compositions, which reveals a variety of compositional trends (library position mapping is shown in figure S4). Particularly distinctive compositions include the Cr–Fe composition line with V concentration between 0.5 and 0.55 where the monoclinic MVO$_4$ (phase field E)
Figure 4. Optical property of Cr–Fe–V oxide system. False-color composition plots of molar absorption coefficient averaged over three different ranges of incident photon energy. The molar absorption coefficient was calculated as the ratio of the unitless absorption coefficient and the molar concentration of metals.

Figure 5. Optical characterization of Cr$_{0.5}$Fe$_{0.5}$VO$_4$-mon photoanode. (a) The normalized transmittance $T$, normalized total reflectance $R$, and absorption coefficient $\alpha$ calculated using the thickness estimated from XRF. (b) Spectral EQE of this sample in sulfite-containing pH 9 electrolyte using four different LEDs (2.1, 2.4, 2.7, and 3.2 eV) at 1.23 V vs RHE, and Tauc signals, where the EQE (left) and the direct allowed (DA) and indirect allowed (IA) Tauc signals each have a dedicated vertical axis. The direct and indirect band gaps are estimated to be 2.6 ± 0.1, and 1.9 eV ± 0.3, respectively, where the uncertainty represents the approximate range of values that may be obtained from manual Tauc analysis.

was observed in figures 1 and 2, which exhibits relatively low absorption. Other compositions containing a mixture of MVO$_4$ with other phases, especially M$_2$O$_3$, exhibit much higher absorption, for example Cr$_{0.2}$Fe$_{0.6}$V$_{0.2}$ in phase field G that exhibits high absorption over the full spectral range.

The optical spectroscopy analysis is combined with the EQE data for the primary composition of interest, Cr$_{0.23}$Fe$_{0.24}$V$_{0.53}$, in figure 5. The spectral transmittance, total reflectance, and absorption coefficient of this sample are shown in figure 5(a). Tauc analysis was used to characterize the band gap, resulting in approximate indirect-allowed and direct-allowed band gap energies of 2 and 2.6 eV, respectively. These values are similar to the band gaps we reported previously for FeVO$_4$, Cr$_2$V$_2$O$_{13}$, CrVO$_4$-orth, and CrVO$_4$-mon photoanodes [12]. The EQE is also plotted in figure 5(b) revealing photoactivity at 2.1 eV, just above the approximate indirect band gap energy. Given the uncertainty in the band gap energy and the relatively low EQE at 2.1 eV, these results are consistent with photoactivity onset from bandgap excitation, although the absorption and photoactivity may also involve mid-gap states, for example from point defects, whose importance is noted in the Discussion. Automated Tauc analysis to observe compositional trends in the approximate direct and indirect band gap energies are shown in figure S5.

3.4. Property variations in the FeVO$_4$–CrVO$_4$ pseudo-binary space

X-ray photoelectron spectroscopy (XPS) was employed for characterization of the near-surface composition of eight MVO$_4$ photoanode samples, spanning Fe/Cr values from 0.34 to 4.1, after their PEC characterization (figure S6). The positions of the Fe 2p, Cr 2p, V 2p, and O 1s peaks do not noticeably vary with Fe/Cr composition. Core level spectra of the transition metals are consistent with the nominal oxidation states Fe$^{3+}$, Cr$^{3+}$, and V$^{5+}$. The O 1s signal contains a high-binding energy peak near 532.4 eV that is presumed to
Table 1. Composition characterization of MVO₄ photoanodes. For a series of eight photoanode samples, the composition measured by XRF before photoelectrochemistry and by XPS after photoelectrochemistry are shown using a the molar ratio X/(Fe + Cr + V) with X = Fe, Cr, V for both XAS and XPS, and additionally X = O for XPS. The formula unit value of this ratio for X = O is 2.

|       | XRF |       |       |       | XPS |       |       |       |
|-------|-----|-------|-------|-------|-----|-------|-------|-------|
|       | Fe  | Cr    | V     |       | Fe  | Cr    | V     | O     |
|       | 0.12| 0.35  | 0.53  |       | 0.15| 0.37  | 0.49  | 1.83  |
|       | 0.18| 0.29  | 0.53  |       | 0.22| 0.31  | 0.47  | 1.87  |
|       | 0.21| 0.26  | 0.53  |       | 0.24| 0.27  | 0.49  | 1.91  |
|       | 0.24| 0.23  | 0.54  |       | 0.25| 0.26  | 0.49  | 1.88  |
|       | 0.26| 0.20  | 0.54  |       | 0.29| 0.22  | 0.48  | 1.92  |
|       | 0.30| 0.18  | 0.53  |       | 0.32| 0.20  | 0.48  | 1.87  |
|       | 0.33| 0.12  | 0.55  |       | 0.36| 0.14  | 0.50  | 1.89  |
|       | 0.37| 0.09  | 0.55  |       | 0.40| 0.11  | 0.49  | 1.90  |

Figure 6. Property variation in the FeVO₄–CrVO₄ pseudo-binary space. (a) The lattice parameters of monoclinic MVO₄ structure (M = Cr,Fe) of a-, b-, and c-axis derived from x-ray diffraction data, (b) EQE percentage under 2.4 and 2.1 eV illumination at 1.23 V vs RHE in sulfite-containing pH 9 electrolyte, (c) the average molar absorption coefficient in the 2.0–2.5 eV photon energy, as a function of Fe to Cr ratio in FeVO₄–CrVO₄ pseudo-binary space.

be from residual electrolyte salt and thus excluded from composition analysis. The primary O 1s signal near 530 eV binding energy is consistent with lattice oxygen in transition metal oxides. The composition analysis of the XPS survey scans is shown in table 1, exhibiting compositions that are within the approximately 10% uncertainty of the formula unit composition and XRF-based cation composition. In particular, the oxygen stoichiometry O/(Fe + Cr + V) is between 1.83 and 1.92 for all samples with no systematic relationship to the Fe–Cr composition.

To visualization the composition–property relationships within the MVO₄ structure, figure 6 combines the results from the structural, PEC, and optical analyses for compositions with V concentration of 0.54 ± 0.01, focusing on the 2–2.5 eV range of greatest interest. XRD peak shifting observed in figure 2 correspond to the lattice constant variation shown in figure 6(a). While lattice constant c keeps almost constant with increasing Fe/Cr, lattice constant a and b increase rapidly at the same rate until Fe/Cr around 3. Further increasing Fe results in the increase of lattice constant c while a and b increase more slowly with increasing Fe/Cr.
The compositions with Fe/Cr near 1, e.g., near Cr$_{0.23}$Fe$_{0.24}$V$_{0.53}$, provide the global maximum for EQE at 2.1 eV, with the Fe/Cr = 1 ± 0.04 compositions exhibiting >2.4× higher EQE that compositions with Fe/Cr > 4, as shown in figure 6(b). The average absorption coefficient shows a decrease with Fe/Cr between 0.3 and 1 and further increasing Fe has no effect on the coefficient.

Quantitative analysis of the internal quantum efficiency (IQE) is best done with in situ measurement of the fraction of absorbed incident light during PEC, which was not performed in the present study. Figures 3, 5, and 6 reveal that the maximal EQE samples are near the minimum in $\alpha$, which indicates that the IQE of the compositions near Cr$_{0.23}$Fe$_{0.24}$V$_{0.53}$ will be substantially higher than the other materials in this composition library. This finding suggests that the equimolar Cr–Fe occupation in the MVO$_4$ structure enhances the charge separation and/or carrier transport efficiency.

4. Discussion

The EQE measurement at 1.23 V vs RHE with 3.2 eV photon illumination is the condition where most binary metal vanadate phases, e.g., FeVO$_4$-tri, Fe$_2$V$_4$O$_{13}$, CrVO$_4$-mon, CrVO$_4$-orth, and Cr$_2$V$_4$O$_{13}$, have been demonstrated to be photoactive in our previous paper [12]. In the Cr–Fe–V oxide system, the presence of multiple photoactive phases with substitutional alloying-based tuning of composition result in detectable photoactivity for most compositions. The only compositions found to be relatively inactive are compositions with V concentration below 0.3 and Cr, Fe concentration between 0.3 and 0.6, where Cr$_2$O$_3$ is the dominate phase. The local maxima in performance with 3.2 and 2.7 eV illumination appear in two regions: (a) near the Fe–V binary line with Cr concentration below 0.1, and Fe concentration between 0.4 (Fe-rich MVO$_4$-mon, phase field E) and 0.6 (the mixture of FeVO$_4$-tri and CeFeO$_3$, phase field I), and (b) at a composition with minimum Fe (<0.1) and V concentration of 0.6 (phase mixture of CrVO$_4$-mon and CrVO$_4$-orth, phase field D), towards more V composition (phase mixture of CrVO$_4$-m and M$_2$V$_2$O$_{13}$, phase field B). These observations are largely consistent with the known Cr and Fe metal vanadate photoanode materials from experiments using broad-band illumination [12–14, 18–22].

While the present high throughput-based discovery cannot uniquely identify the mechanism underlying the improved performance provided by the equal population of Fe and Cr on the M site of the MVO$_4$ structure, the combinatorial data can provide guidance for future mechanistic studies. In the monoclinic BiVO$_4$ system, one demonstrated benefit of substitutional alloying is lowering of the monoclinic distortion to facilitate carrier transport [47]. While figure 6(a) show considerable lattice constant modulation with Fe–Cr composition, there is no apparent structural parameter with maximal value corresponding to the maxima in the EQE data of figure 6(b). The analysis of carrier lifetime and mobility by Zhang et al indicated that FeVO$_4$ carrier transport is in the carrier-tunneling regime wherein a high density of recombination centers enables tunneling from a trapped carrier site to a nearby recombination site [22]. Figure 57 provides circumstantial evidence for a high concentration of recombination centers in the Fe-rich MVO$_4$ samples with the observation of substantial current transients upon illumination. The time resolution of the present data does not afford detailed modelling of the current transients, but their intensity decreases with increasing Cr concentration. Such current transients are typically attributed to population of surface states, and their persistence in the presence of a sacrificial hole acceptor is commensurate with the extension of these states into the bulk of the semiconductor. This observation points toward the need to understand the extent by which Cr substitutions mitigate mid-gap states and the associated density of recombination centers. One mechanism by which this may occur is by lowering the concentration of oxygen vacancies, which have been demonstrated to be central to carrier transport and surface chemistry of BiVO$_4$ and other metal oxides [48, 49]. Notably the XPS characterization of O concentration has neither the precision nor the penetration depth to ascertain defect-level changes in the oxygen stoichiometry of the thin film photoanodes.

The combinatorial synthesis of a broad range of composition coupled with high throughput synchrotron diffraction and spectrally-resolved EQE measurements reveals the composition region that performs well over a broader spectral range, the MVO$_4$ structure with composition near (Cr$_{0.5}$Fe$_{0.5}$)VO$_4$-mon. The compositions near the local maximum in EQE in phase field D from 3.2 and 2.7 eV illumination are inactive at lower photon energies, demonstrating that non-spectrally-resolved measurements at the materials discovery stage can miss the most promising materials for further development, especially toward the development of a photoanode that utilizes lower-energy photons than state-of-the-art photoanode BiVO$_4$.

5. Conclusion

A series of M–V–O and M–O phases (M = Cr,Fe), and mixtures thereof, were fabricated by combinatorial synthesis, where all phases of interest exhibit Fe–Cr substitutional alloying on the M sublattice. High throughput XRD, photoelectrochemistry, and optical spectroscopy were combined to study the composition
and structure-based variation in properties pertinent to solar fuels photoanodes. FeVO₄ and CrVO₄-based photoanodes have been investigated for improving upon the state-of-the-art BiVO₄ by utilizing the 2–2.4 eV portion of the solar spectrum, and the present work indicates that the substitutional alloy phase (CrₓFeₓ)₀.₅VO₄ provides the greatest opportunity for developing next-generation photoanodes.

Data availability statement

The data that support the findings of this study are openly available at the following URL/DOI: https://data.caltech.edu/records/20061.

Acknowledgments

This work is based on data collected at the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, Fuels from Sunlight Hub under Award DE-SC0021266. Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. The authors thank Apurva Mehta and Douglas Van Campen for assistance with the synchrotron experiments and Aniketa Shinde, Paul F Newhouse, and Santosh K Suram for assistance will collection of the materials characterization data.

ORCID iDs

Lan Zhou https://orcid.org/0000-0002-7052-266X
Dan Guevarra https://orcid.org/0000-0002-9592-3195
John M Gregoire https://orcid.org/0000-0002-8683-5265

References

[1] Walter M G, Warren E L, McKone J R, Boetcker S W, Mi Q, Santori E A and Lewis N S 2010 Solar water splitting cells Chem. Rev. 110 6446–73
[2] Hu S, Xiang C, Haussener S, Berger A D and Lewis N S 2013 An analysis of the optimal band gaps of light absorbers in integrated tandem photovoltaic-photoelectrochemical water-splitting systems Energy Environ. Sci. 6 2984–93
[3] Fountaine K T, Lewerenz H J and Atwater H A 2016 Efficiency limits for photovoltaic-photoelectrochemical water-splitting Nat. Commun. 7 13706
[4] Park Y, McDonald K J and Choi K-S 2013 Progress in bismuth vanadate photoanodes for use in solar water oxidation Chem. Soc. Rev. 42 2321–37
[5] Tan H L, Amal R and N S H 2017 Alternative strategies in improving the photocatalytic and photoelectrochemical activities of visible light-driven BiVO₄: a review J. Mater. Chem. A 5 16498–521
[6] Abdi F F and Berglund S P 2017 Recent developments in complex metal oxide photoelectrodes J. Phys. D: Appl. Phys. 50 193002
[7] Lee D K, Lee D, Lumley M A and Choi K-S 2019 Progress on ternary oxide-based photoanodes for use in photoelectrochemical cells for solar water splitting Chem. Soc. Rev. 48 2126–57
[8] He H, Liao A, Guo W, Luo W, Zhou Y and Zou Z 2019 State-of-the-art progress in the use of ternary metal oxides as photocathode materials for water splitting and organic synthesis Nano Today 28 100763
[9] Jiang C, Wang R and Parkinson B A 2013 Combinatorial approach to improve photocathode based on BiVO₄ ACS Comb. Sci. 15 639–45
[10] Toma F M et al 2016 Mechanistic insights into chemical and photochemical transformations of bismuth vanadate photoanodes Nat. Commun. 7 12012
[11] Sharp J D, Cooper J K, Toma F M and Buonsanti R 2017 Bismuth vanadate as a platform for accelerating discovery and development of complex transition-metal oxide photoanodes ACS Energy Lett. 2 139–50
[12] Yan Q et al 2017 Solar fuels photoanode materials discovery by integrating high-throughput theory and experiment Proc. Natl Acad. Sci. 114 3040–3
[13] Mandal H, Shyamal S, Hajra P, Bera A, Sariket D, Kundu S and Bhattacharya C 2016 Development of ternary iron vanadium oxide semiconductors for applications in photoelectrochemical water oxidation RSC Adv. 6 4992–9
[14] Tang D, Rettie A J E, Mahayoe O, Wygant B R, Lai Y, Liu Y and Mullins C B 2016 Facile growth of porous Fe₄V₆O₁₃ films for photoelectrochemical water oxidation J. Mater. Chem. A 4 3034–42
[15] Zhang L, Zhou J and Zhang C 2014 pH-controlled growth of ultrathin iron vanadium oxide (Fe₄V₆O₁₃) nanoplatelets with high visible-light photo-catalytic activity J. Mater. Chem. A 2 14903–7
[16] Araú J, Korinish Y, Iwasaki Y, Sugiwar H and Sayama K 2007 High-throughput screening using porous electrode for the development of visible-light-responsive semiconductors J. Comb. Chem. 9 574–81
[17] Morton C D, Slipper I J, Thomas M J K and Alexander B D 2010 Synthesis and characterisation of Fe₃V₄O₁₁ thin film photoanodes J. Photochem. Photobiol. A 216 209–14
[18] Biswas S K and Baeg J-O 2013 Enhanced photoactivity of visible light responsive W incorporated FeVO₄ photoanode for solar water splitting Int. J. Hydrog. Energy 38 14451–7
[19] Wang W, Zhang Y, Wang L and Bi Y 2017 Facile synthesis of Fe³⁺/Fe²⁺ self-doped nanoporous FeVO₄ photoanodes for efficient solar water splitting J. Mater. Chem. A 5 2478–82
[20] Feng J, Wang Z, Zhao X, Yang G, Zhang B, Chen Z and Huang Y 2018 Probing the performance limitations in thin-film FeVO₄ photoanodes for solar water splitting J. Phys. Chem. C 122 9773–82
[21] Kumari S, Gutkowski R, Junqueira J R C, Kostka A, Hengge K, Scheu C, Schuhmann W and Ludwig A 2018 Combinatorial synthesis and high-throughput characterization of Fe–V–O thin-film materials libraries for solar water splitting ACS Comb. Sci. 20 544–53
[22] Zhang M, Ma Y, Friedrich D, van de Krol R, Wong L H and Abdi F F 2018 Elucidation of the opto-electronic and photoelectrochemical properties of FeVO₄ photoanodes for solar water oxidation J. Mater. Chem. A 6 548–55
[23] Li Y, Liu G, Jia D, Li C, Wang L, Zheng J, Liu X and Jiao Z 2019 Nanoporous FeVO₄ photoanodes modified with ultrathin C₆N₆ for high photoelectrochemical water splitting performance Catal. Lett. 149 19–24
[24] Chang S, Wang M, Wang C-C, Fu X, Bi H and Zeng Q 2021 FeVO₄ nanopolyhedron photoelectrodes for stable and efficient water splitting ChemSusChem 14 3010–7
[25] Long X, Gao L, Li F, Hu Y, Wei S, Wang C, Wang T, Jin J and Ma J 2019 Bamboo shoots shaped FeVO₄ passivated ZnO nanorods photoanode for improved charge separation/transfer process towards efficient solar water splitting Appl. Catal. B 257 117813
[26] Wu J, Guo W, Ding Z, Zhang J and Hou Y 2021 An ultrathin TiO₂ interfacial layer enhancing the performance of an FeVO₄ photoanode for water splitting Sustain. Energy Fuels 5 261–6
[27] Nguyen T H, Zhang M, Septina W, Ahmed M G, Tay Y F, Abdi F F and Wong L H 2020 High throughput discovery of effective metal doping in FeVO₄ for photoelectrochemical water splitting Sol. RRL 4 2000437
[28] Bera G, Mal P, Reddy V R, Deshpande U, Das P, Padmaja G and Turpu G R 2020 Vibrational spectra and optical properties of Fe₀₋ₓCrₓVO₄ solid solutions: with a group theory analysis Spectrosc. Acta A 227 117668
[29] Errandonea D and Garg A B 2018 Recent progress on the characterization of the high-pressure behaviour of AVO₄ orthovanadates Prog. Mater. Sci. 97 123–69
[30] Bera G, Reddy V R, Rambabu P, Mal P, Das P, Mohapatra N, Padmaja G and Turpu G R 2017 Triclinic–monoclinic–orthorhombic (T–M–O) structural transitions in phase diagram of FeVO₄−CrVO₄ solid solutions J. Appl. Phys. 122 115101
[31] Lavat A E, Grasselli M C and Baran E J 1989 The IR spectra of the (Cr₃Feₓ−₃)VO₄ phases J. Solid State Chem. 78 206–8
[32] Attfield J, P, Cheetah A K, Johnson D C and Novet T 1991 Magnetic frustration, spirals and short-range order in CrₓFe₋ₓVO₄-I solid solutions J. Mater. Chem. 1 867–73
[33] Bera G, Surampalli A, Mishra A, Mal P, Reddy V R, Banerjee A, Sagdeo A, Das P and Turpu G R 2019 Magnetolattice coupling, magnetic frustration, and magneto-electric effect in the Cr-doped FeVO₄ multiferroic material and their correlation with structural phase transitions Phys. Rev. B 100 014436
[34] Zhang M, Pham H K, Fang Y, Tay Y F, Abdi F F and Wong L H 2019 The synergistic effect of cation mixing in mesoporous BiₓFe₋ₓVO₄ heterojunction photoanodes for solar water splitting J. Mater. Chem. A 7 14816–24
[35] Kurzawa M 1990 Reactivity of CrVO₄ with FeVO₄ J. Thermal Anal. 36 2181–5
[36] Tabero P and Filipke E 2001 Synthesis and properties of the solid solutions formed in the Fe₂Vₓ₁−xO₄ system J. Therm. Anal. Calorim. 64 1067–72
[37] Suram S K, Zhou L, Becerra-Stasiewicz N, Kan K, Jones R J, Kendrick B M and Gregoire J M 2015 Combinatorial thin film composition mapping using three dimensional deposition profiles Rev. Sci. Instrum. 86 033904
[38] Gregoire J M, Zhou L and Guevarra D 2022 Recent progress on the characterization of the high-pressure behaviour of AVO₄ orthovanadates Prog. Mater. Sci. 97 123–69
[39] Lavat A E, Grasselli M C and Baran E J 1989 The IR spectra of the (Cr₃Feₓ−₃)VO₄ phases J. Solid State Chem. 78 206–8
[40] Attfield J, P, Cheetah A K, Johnson D C and Novet T 1991 Magnetic frustration, spirals and short-range order in CrₓFe₋ₓVO₄-I solid solutions J. Mater. Chem. 1 867–73
[41] Bera G, Surampalli A, Mishra A, Mal P, Reddy V R, Banerjee A, Sagdeo A, Das P and Turpu G R 2019 Magnetolattice coupling, magnetic frustration, and magneto-electric effect in the Cr-doped FeVO₄ multiferroic material and their correlation with structural phase transitions Phys. Rev. B 100 014436
[42] Zhang M, Pham H K, Fang Y, Tay Y F, Abdi F F and Wong L H 2019 The synergistic effect of cation mixing in mesoporous BiₓFe₋ₓVO₄ heterojunction photoanodes for solar water splitting J. Mater. Chem. A 7 14816–24
[43] Mitrović S, Cornell E W, Marcin M R, Jones R J R, Newhouse P F, Suram S K, Jin J and Gregoire J M 2015 High-throughput on-the-fly scanning ultraviolet-visible dual-sphere spectrometer Rev. Sci. Instrum. 86 013904
[44] Gregoire J M, Xiang C, Liu X, Marcin M and Jin J 2013 Scanning droplet cell for high throughput electrochemical and photoelectrochemical measurements Rev. Sci. Instrum. 84 024102
[45] Zhou L, Shinde A, Newhouse P F, Guevarra D, Wang Y, Lai Y, Kan K, Suram S K, Haber J A and Gregoire J M 2020 Quaternary oxide photoanode discovery improves the response spectrum and photovoltaic of copper vanadates Mater. 3 1614–30
[46] Sliozberg K, Stein H S, Khare C, Parkinson B A, Ludwig A and Schuhmann W 2015 Fe–Cr–Al containing oxide semiconductors as potential solar water-splitting materials ACS Appl. Mater. Interfaces 7 4883–9
[47] Kumari S, Junqueira J R C, Sarker S, Mehta A, Schuhmann W and Ludwig A 2020 Structural and photoelectrochemical properties in the thin film system Cu–Fe–V–O and its ternary subsystems Fe–V–O and Cu–V–O J. Chem. Phys. 153 014707
[48] Chen D, Bai Y, Ament S, Zhao W, Guevarra D, Zhou L, Selman B, van Dover R B, Gregoire J M and Gomes C P 2021 Automating crystal-structure phase mapping by combining deep learning with constraint reasoning Nut. Mach. Intell. 3 812–22
[49] Gong H, Freudenberg N, Nie M, van de Krol R and Ellmer K 2016 FeVO₄ photoanodes for water splitting with high injection efficiency, deposited by reactive magnetron co-sputtering AIP Adv. 6 045108
[50] Newhouse P F et al 2018 Combinatorial alloying improves bismuth vanadate photoanodes via reduced monoclinic distortion Energy Environ. Sci. 11 2444–57
[51] Talavarthi R, Zboril R, Schmuki P, Naldoni A and Kment S 2021 Elucidating the role of surface states of BiVO₄ with Mo doping and a CoOOH co-catalyst for photoelectrochemical water splitting J. Power Sources 483 229080