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To cite this article: Joseph T. English and David P. Wilkinson 2021 J. Electrochem. Soc. 168 103509

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The Superior Electrical Conductivity and Anodic Stability of Vanadium-Doped TiO$_7$

Joseph T. English$^{1,2,*}$ and David P. Wilkinson$^{1,2,##}$

$^1$Department of Chemical and Biological Engineering, University of British Columbia, Vancouver, BC V6T 1Z3, Canada
$^2$Clean Energy Research Centre, University of British Columbia, Vancouver, BC V6T 1Z3, Canada

The effectiveness of Magnéli phase titanium oxides (Ti$_n$O$_{2n-1}$, 4 $\leq$ n $\leq$ 10), promising alternatives to carbon-based materials in aqueous electrochemical technologies, is limited by their instability at strongly oxidizing electrode potentials. Ti$_4$O$_7$ and Ti$_5$O$_9$, the most electrically-conductive Ti$_n$O$_{2n-1}$, passivate in the harsh conditions demanded by fuel cells, batteries, and devices for the electrochemical treatment of water. Among other properties relevant to electrodes, doping of Ti$_n$O$_{2n-1}$ with transition metals vanadium, chromium, and iron improves the oxidation stability as demonstrated by higher onset temperatures in the thermograms of doped Ti$_6$O$_{12}$ heated in air. To investigate the influence of doping on their anodic stability, disk electrodes of Ti$_6$O$_{12}$ doped with V, Cr, and Fe were investigated by electrochemical accelerated life testing (ALT). These disks, prepared by high-temperature H$_2$ reduction of nominally 2 at% doped titanium(IV) oxide (TiO$_2$), were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectroscopy, X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (PXRD), the 4-point probe method, cyclic voltammetry (CV), Tafel plot analysis, and electrochemical impedance spectroscopy (EIS). V- and Fe-doping are shown to improve the electrical conductivity and V-doping is demonstrated to improve the anodic stability as measured by the mean time-to-failure (TTF) during electrochemical ALT.

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Manuscript submitted June 22, 2021; revised manuscript received October 7, 2021. Published October 29, 2021.

Supplementary material for this article is available online

Ti$_4$O$_7$ and Ti$_5$O$_9$, the most electrically-conductive members of the Magnéli phase titanium oxides (Ti$_n$O$_{2n-1}$, 4 $\leq$ n $\leq$ 10), are promising alternatives to carbon-based materials in aqueous electrochemical technologies,5-6 showing excellent electrical conductivity,1 good chemical inertness,7 and a high overpotential for the oxygen evolution reaction (OER).8 While kinetically stable at standard temperature and pressure,9 passivation forming the thermodynamically-favored TiO$_2$ occurs under sufficiently oxidizing conditions (Eq. 1, $E^\circ$ = -0.545 V vs SHE for n = 4).10 This passivation may concern the operation of batteries11 fuel cells,12 and the electrochemical treatment of wastewater.13 Strategies to stabilize these materials against electrochemical oxidation are therefore needed in order to improve the resilience of technologies employing Ti$_n$O$_{2n-1}$-based materials.

\[
\text{Ti}_n\text{O}_{2n-1} + \text{H}_2\text{O} \rightarrow n\text{TiO}_2 + 2\text{H}^+ + 2e^- \tag{1}
\]

Magnéli phase titanium oxides including Ebonex®, a trade name for electrodes based on such materials, have been incorporated into fuel cells (FCs) and water electrolyzers (WEs) for H$_2$ production to great effect. H$_2$O$_2$ proton-exchange membrane (PEM) FCs with membrane electrode assemblies using Ti$_6$O$_{12}$-supported Pt and Nafion ionomer as both anode and cathode catalyst layers exhibit superior anodic stability as compared to Vulcan XC-72.14-16 IrO$_2$ catalyst loaded Ti$_6$O$_{12}$-1 with Nafion ionomer forming the anode catalyst layer of a MEA were used in a PEMWEs, showing improved electrocatalytic activity relative to commercial materials17 and catalyst-coated membranes.18 However, 7 hours of anodic conditioning at 1.6 V (v.s. SHE) of electrodes of Ebonex®-supported Pt$_3$Ru$_4$Ir$_1$, a bifunctional electrocatalyst, results in the irreversible passivation with TiO$_2$ forming Ti$_2$O$_3$.19 Properties relevant to the application of Ti$_n$O$_{2n-1}$ as electrode materials can be modified by doping, including electrical,20 tribological,21 electronic,22 electrocatalytic,23-26 thermal oxidative,27-29 photocatalytic,30,31 and thermolectric properties.32-34 This approach is broadly used to modify the properties of other titanium oxides. For example, Ta, Nb, and In doping of TiO$_2$ is shown to improve the cyclability and discharge capacity of Na-ion battery anodes by expanding the diffusion path and improving the electronic conductivity.35-37 Doping Ti$_4$O$_7$ with Mo, Si, and N yields carbon-free fuel cell electrocatalyst supports with stability and durability.38-40 Recently, it has been demonstrated that doping Ti$_3$O$_7$ with transition metal atoms V, Cr, and Fe increases its stability toward thermal oxidation in air as expressed by the onset temperature obtained by thermogravimetric analysis.9 The kinetics of the thermal oxidation of Ti$_n$O$_{2n-1}$ in air forming TiO$_2$ being a diffusion-controlled process, is hindered by doping, improving its resistance to oxidation. Doping Ti$_4$O$_7$ with the rare-earth metal Ce may also improve the service lives of electrodes as determined by electrochemical accelerated life testing (ALT).29 Therefore, any improvement of the anodic stability of Ti$_n$O$_{2n-1}$ due to V-, Cr-, and Fe-doping must be investigated in an effort to address the aforementioned issues of passivation.

ALT provides a rapid measure of the stability of electrodes such as those for the OER.41-44 In a typical measurement, an electrode is subjected to demanding conditions, including harsh electrolyte, strongly oxidizing or reducing electrode potentials, high current densities, and extreme temperatures—accelerating its time-to-failure (TTF). For mixed-metal oxide coated titanium electrodes used for the OER and the chlorine evolution reaction, TTFs at two different conditions indicated by subscripts 1 and 2 where only the current density ($j$) varies is related by a power law expression (Eq. 2, $1.4 < t < 2.0$).31,42,47

\[
\text{TTF}_1/\text{TTF}_2 = (j_1/j_2)^{t-1} \tag{2}
\]

In this fashion, increasing the current density used during an electrochemical ALT changes the TTF by orders of magnitude.

To investigate the influence of doping on the anodic stability of Ti$_6$O$_{12}$, we prepared disks of pristine and doped Ti$_6$O$_{12}$ and subjected them to electrochemical ALT. Ti$_6$O$_{12}$ disks were obtained by a high-temperature H$_2$ reduction of sintered TiO$_2$ disks and characterized by scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectroscopy, X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS), powder X-ray diffractometry (PXRD), 4-point probe method, cyclic voltammetry (CV), Tafel plot analysis, and electrochemical impedance spectroscopy (EIS).

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$^*$Electrochemical Society Student Member.
$^##$Electrochemical Society Member.
$^4$E-mail: david.wilkinson@ubc.ca
Experimental

Materials.—The following chemicals were used as received: CrCl3·6H2O (purum p.a., 98%, Sigma Aldrich), ethanol (EtOH, pure un-denatured, 100%, University of British Columbia Department of Chemistry), FeCl3 (ACS, 98%, anhydrous, Fisher Chemical), H2SO4 (Certified ACS Plus, 95%–98%, Fisher Chemical), K2SO4 (Certified ACS, 99.2%, Fisher Chemical), titanium tetraisopropoxide (TTIP, 97%, Sigma-Aldrich), and VCl3 (97%, Sigma-Aldrich). Ultrapure water (18.2 MΩ cm) was generated as needed using a laboratory water system (Milli-Q Integral 5, EMD Millipore). Appropriate amounts of CrCl3·6H2O, FeCl3, and VCl3 were dissolved in H2O to obtain 2 M solutions. Pristine and nominally 2 at% doped TiO2 were prepared by diluting appropriate amounts of H2SO4 and K2SO4 in H2O, respectively.

Electrode preparation.—Ar (Ultra High Purity 5.0, 99.999%) and H2 (Ultra High Purity 5.0, 99.999%, Praxair), heavy mineral oil (0.83 g ml⁻¹, FCC/USP, Fisher Scientific), and paraffin wax (mp 58–62 °C, ASTM D 87, Sigma-Aldrich) were used as received. In a typical preparation yielding 5 mm diameter disks, 8 ml of heavy mineral oil as binder was mixed into 0.25 g of pristine or nominally 2 at% doped TiO2. The mixture was then compressed in a 5 mm pellet die (GS03060, Specac) with a 2.00-ton load (910 MPa) using a desktop dry pressing machine (YLI-24TS, MTI Corporation). The compressed disk was then heated in air in a muffle furnace (Type 48 000, Barnstead Thermolyne) to 1,200 °C for 1 hour to remove the binder and sinter the powder. Sintered disks then reduced in H2 at high temperature following a previously-described method. Reduced disks were fitted into an rotating disk electrode (RDE) tip with an interchangeable disk option (ACE4THQ050, Pine Research Instrumentation) and fixed in place with epoxy (Gorilla Epoxy, Gorilla Glue). Fixed disk electrodes were then operated with molten paraffin wax at 80 °C. Sealed disk electrodes were then polished sequentially with 600 grit sandpaper (Carbimet, Buehler), 0.3 micron alumina suspension (90-187510, Allied High Tech Products) on nylon cloth (Nylon, Buehler), then 0.05 micron alumina suspension (90-187505, Allied High Tech Products) on rayon cloth (MicroCloth, Buehler). Polished electrodes were inserted into a body (ACE4TB, Pine Research Instrumentation), attached to a shaft (AFE3M, Pine Research Instrumentation) and silver two part conductive adhesive (Alfa Aesar), and rinsed with ultrapure water prior to the assembly of electrochemical cells.

Physicochemical characterization.—Scanning electron microscopy and energy-dispersive X-ray spectroscopy.—Surface morphology and elemental analysis were obtained using a field emission gun scanning electron microscope (PEI Quanta 650, Thermo Scientific) with an EDX detector accessory (XFLASH 6130, Bruker). All images and EDX spectra were obtained using an accelerating voltage of 20 kV and a working distance of 10 mm. Elemental analysis of EDX spectra was performed using micro-analysis software (ESPIRIT, Bruker, ver. 2.1.2).

X-ray photoelectron spectroscopy.—Surface analyses including elemental composition and chemical state were performed by XPS with a X-ray photoelectron spectrometer (Axis Ultra DLD, Kratos Analytical) using a monochromatic Al X-ray source and a hemispherical analyzer. Prior to acquisition, the samples were etched with a monatomic Ar⁺ ion source (Minibeam 4, Kratos Nalytical) having a beam energy of 3 keV for 5 minutes. Step size, dwell time, and sweeps were 1 eV, 0.8 s, and 2 for survey spectra; 0.1 eV, 0.5 s, and 2 for high resolution spectra of Ti 2p and O 1s, and 0.1 eV, 1.0 s, and 5 for high resolution spectra of V 2p and Fe 2p, respectively. XPSPEAK (Raymond W. M. Kwok, Chinese University of Hong Kong, ver. 4.1) was used to process constituent peaks within high-resolution data using Shirley backgrounds. Peak assignments were made by comparison with published data compiled in the NIST X-ray Photoelectron Spectroscopy Database (ver. 4.1).

Powder X-ray diffractometry.—Phase identification and structure refinement was conducted with PXRD data obtained using a Bragg-Brentano theta–theta geometry X-ray diffractometer (Phaser D2, Bruker) with a Cu X-ray source (1.5406 Å) and a Si strip detector (LYNXEYE, Bruker). Prior to acquisition, disks were manually ground with an agate mortar and pestle forming a powder. In a typical measurement, a powder sample was illuminated with radiation from the X-ray source excited at 30 kV with 10 mA passing through a 1.0 mm primary slit module, 2.5° stoller module, and a 0.5 mm Ni filter using a step size of 0.02° and an integration time of 1 s. Phase identification was carried out using the instrument software (DIFFRAC.EVA, Bruker) with reference to the Crystallography Open Database (COD), later generating patterns using VESTA crystallography software (ver. 3.4.7) and relevant Crystallographic Information Files (CIFs).

4-point probe method.—Electrical conductivity (σ) was evaluated from resistance data generated using the 4-point probe method with manual four point probe resistivity probing equipment (S-302-4, Signatone) and a standard head (SP4-40045TRY, Signatone). In a typical measurement, the head was brought into contact with a stationary RDE and a 1 kHz AC test current with an amplitude of 100 mA was generated using a multichannel electrochemical workstation (VMP3, BioLogic). The real component of the measured impedance (VII) was used to evaluate the electrical conductivity using the reciprocal of the 4-point probe equation for evaluating resistivity (Eq. 3) where s is the tip spacing (0.10 cm) and F is the correction factor (Eq. 4).

\[
\sigma = \frac{2\pi s (V/I) F^{-1}}{F = F_1 F_2 F_3}
\]

Electrochemical measurements.—A multichannel electrochemical workstation (VMP3, BioLogic) and a standard 150 ml cell (AKCELL2, Pine Research Instrumentation) using an undivided conventional 3-electrode setup were used for all electrochemical measurements. A saturated mercury mercourous sulfate reference electrode (XR200, Radiometer Analytical) with saturated aqueous K2SO4 as its secondary solution and a platinum foil counter electrode (M241Pt, Radiometer Analytical) were used for all measurements. The potential of the reference electrode was measured at open circuit with a normal hydrogen electrode (NHE) constructed using platinum foil in 0.5 M H2SO4 saturated with H2 (pH 0.4, 22 °C). The disk electrodes were rotated at 2,000 RPM
using an electrode rotator (AFMSRCE, Pine Research Instrumentation) to assist in the removal of evolved gases from the electrode surface. Tafel plot data were obtained by averaging the final 5 s of 10 s galvanostatic measurements. EIS conducted intermittently during ALT was done galvanostatically with a 100 mA cm⁻² current at an amplitude of 1 mA cm⁻². All potentials were corrected using the uncompensated resistance determined by EIS at 100 kHz at open circuit with a 20 mV amplitude.

Results and Discussion

Disks are porous and highly-doped Ti₄O₇—The color of the powders prior to compression into a disk suggests that the dopant is incorporated into the TiO₂, consistent with previous preparations. After compression, sintering, and H₂ reduction, the disks are dark blue in color (Fig. 1a), consistent with the preparation of Ti₄O₇₋₁. The estimated bulk density (\(ρ_{\text{bulk}}\)) of these disks is similar given the masses and dimensions of the samples (parenthetical values indicate uncertainties of final digit): 2.6(2), 3.1(3), 2.7(3), and 2.8(2) g cm⁻³ for pristine, V-, Cr-, and Fe-doped samples, respectively. Considering the true density (\(ρ\)) of Ti₄O₇ (4.32 g cm⁻³), the average porosity (\(ε\), Eq. 5) of the samples prior to sealing with molten wax is evaluated to be 35 ± 4%, which is consistent with random close packing. Scanning electron micrographs (Figs. 1b–1e) illustrate the morphology of the disks typical of monolithic Ti₄O₇₋₁. The disks are composed of micrometer-sized particles, which are fused to one another, as well as many voids and holes, consistent with the predicted porosity. The particles in the doped samples appear to be marginally larger than those in the pristine material. This minor size discrepancy has also been observed in powder preparations, where it is speculated that the metal halide in the sol act may act as a peptizing agent.

\[ ε = 1 - \frac{ρ_{\text{bulk}}}{ρ} \]  

Statistical analysis of the data obtained by EDX spectroscopy and XRF analysis of the H₂-reduced pristine and nominally 2 at% TiO₂ disks (Table I) suggests that the dopants are present at approximately 2 at%. EDX spectroscopy results are equivalent or marginally lower than expected values whereas XRF results are equivalent to the expected values. This disparity is attributed to systematic errors in the preparation and storage of the transition metal halide solutions, the quality of the TTIP reagent, and its volatilization during the aging step of the sol-gel process. Attempts to conduct elemental mapping SEM images with EDX spectroscopy were unsuccessful. It is suspected that the accelerating voltage was too high to provide sufficient spatial resolution. Analysis of survey spectra obtained by XPS of the disks (Fig. 2a) identifies dopants V and Fe in their respective samples; the presence of Cr dopant could not be unambiguously identified due to the overlap of its 2p peak with the Ti 2s peak. Deconvolution of high resolution spectra of V 2p₃/₂ and Fe 2p₃/₂ peaks (Figs. 2b & 2c, Table SI) suggests that the oxidation states are V⁵⁺/V³⁺ and Fe²⁺/Fe⁶⁺. And while earlier-reported analysis of structural refinement of PXRD data suggested the presence of a metallic iron phase in Fe-doped Ti₄O₇, deconvolution of the Fe 2p₃/₂ peak does not provide support of this postulation. Deconvolution of the Ti 2p and O 1s peaks (Fig. S1, Tables SI & SII) suggests that Ar ion etched surface is reduced relative to untreated materials (cf. 9). It is unclear, however, whether this is representative of the underlying material or the result of Ar ion damage to the surface. Nobel gas ion bombardment is reported to reduce surfaces of TiO₂ due to a preferential etching of oxygen. Valence band spectra of Ar ion etched samples (Fig. S2) reveal the presence of surface states above the valence band, consistent with the reduction of TiO₂ by Ar ion etching.

Phase identification analysis of the patterns obtained by PXRD (Fig. 3) provides evidence to suggest that the H₂-reduced pristine and doped TiO₂ disks are monophasic Ti₄O₇. Specifically, a pattern typical of Ti₄O₇ can be seen with intense peaks at 20.8° and 31.8° 2 theta. The presence of a subtle broad peak in the baseline can be representative of the underlying material or the result of Ar ion damage to the surface. Valence band spectra of Ar ion etched samples (Fig. S2) reveal the presence of surface states above the valence band, consistent with the reduction of TiO₂ by Ar ion etching.

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V- and Fe-doping improve electrical conductivity. —V- and Fe-doped TiO₂ samples exhibit significantly greater electrical conductivities (σ, Table II) than pristine samples as determined from resistances measured by the 4-point probe method. The electrical conductivities of pristine samples are approximately an order of magnitude lower than single-crystal measurements (1,300–1,900 S cm⁻¹). The relatively lower electrical conductivity is attributed to the preponderance of grain boundaries in the samples as well as porosity (vide supra). However, these electrodes have conductivities comparable to nonpermeable grade Ebonex® electrodes (100–1,000 S cm⁻¹), the trade name for Ti₅O₂₂⁻₁-based electrodes, and are approximately an order of magnitude greater than monolithic TiO₂ reactive electrochemical membranes (REMs, 11.32–13.49 S cm⁻¹). As the pristine and doped samples are morphologically similar, the superior electrical conductivities demonstrated by V- and Fe-doped samples are attributed to the presence of their respective dopants. Schlenker et al. observe a variation in the electrical resistivity of V-doped TiO₂, with the highest doped (1.64 at%) sample investigated being the least resistive. The authors suggest that vanadium contributes little to the scattering of charge carriers due to the already large concentration of scattering centers in the pristine material. As the carrier mobility is likely unaffected, it is postulated that the superior electrical conductivity of these materials must therefore be due to an increase in the carrier concentration. While Gusev et al. observe a relatively diminished electrical conductivity in V- (1.5 wt% V₂O₅) and Fe-doped (1.36 wt% Fe) Ti₅O₂₂⁻₁, these samples contain multiple phases, whose electrical conductivities also vary considerably.

Electrocatalytic behavior for water splitting reactions unaffected by V- and Cr-doping. —Cyclic voltammograms of pristine and doped TiO₂ disk electrodes in 0.5 M H₂SO₄ is typical of Ti₅O₂₂⁻₁-based electrodes (Fig 4). Pristine and doped TiO₂ disk electrodes show a wide potential window of >3 V as measured by the onset potential for anodic and cathodic currents unambiguously attributable to the OER and the hydrogen evolution reaction (HER), respectively. For this qualitative metric, potentials at current densities of ±10 mA cm⁻² were chosen; however, this methodology is highly varied in literature, including the use of different linear potential scan rates, current densities, supporting electrolyte, and supporting electrolyte concentration. The wide potential window of Ti₅O₂₂⁻₁-based electrodes is due to their poor electrocatalytic properties for the OER and HER, requiring large overpotentials—most markedly for the OER. The potential window for the Fe-doped sample is the largest, suggesting that dopant incorporation is inhibiting its electrocatalytic behavior toward the water splitting reactions with greater overpotentials required for both. Cathodic and anodic peaks found at negative potentials in the CVs are attributed to reduction and oxidation of the TiO₂ film, consistent with the behavior of Ebonex® electrodes. At potentials greater than these peaks, there is an absence of prominent redox features with the exception of the Fe-doped sample, whose CV shows a small plateau around 2 V (vs NHE). It is speculated that this feature may be due to the oxidation of the electrode surface. This oxidation may also contribute to the passivation of the Fe-doped electrode explaining the relatively large overpotential for the OER due to a reduced electrochemically-active surface area (ECSA). The ECSA can be estimated based on the charging current in a region of the voltammogram devoid of prominent redox features. The ECSA is determined by Eq. 6, where I₄ and I₅ are the anodic and cathodic currents, respectively, at some fixed potential; Ageo is the geometric area of the electrode; (0.196 cm²) geos NHE, the ECSA of pristine, V-, Cr-, and Fe-doped disks does not significantly differ having estimated values of 17 ± 4, 10 ± 3, 14 ± 3, and 12 ± 3 cm² ECSA. Based on the charging current between potentials 1 and 2 V (vs NHE), the ECSA of pristine, V-, Cr-, and Fe-doped disks does not significantly differ having estimated values of 17 ± 4, 10 ± 3, 14 ± 3, and 12 ± 3 cm² ECSA. (5 observations, 5% confidence level), respectively. Based on these ECSAs, the electrodes have a roughness factor of 68 ± 24, which is an order of magnitude lower than similarly-prepared porous TiO₂ electrodes, suggesting that the molten wax...

**Table I. Summary of statistical analysis (5 observations, 5% significance level) of energy-dispersive X-ray (EDX) spectroscopy and X-ray fluorescence (XRF) of dopant in H₂-reduced pristine and nominally 2 at% doped TiO₂ disks.**

| Dopant | EDX       | XRF       |
|--------|-----------|-----------|
| Vanadium | 1.6 ± 0.1 | 2.0 ± 0.4 |
| Chromium | 1.5 ± 0.1 | 2.1 ± 0.3 |
| Iron    | 2.4 ± 0.4 | 2.0 ± 0.4 |

Example Figure:

**Figure 2.** X-ray photoelectron spectra of Ar-ion etched (4 keV) H₂-reduced pristine and nominally 2 at% doped TiO₂ disks: (a) survey spectra and high resolution spectra of (b) V 2p and (c) Fe 2p peaks.
has filled most of the inner porous structure.

The ECSA is given by

$$\text{ECSA} = \frac{(I_s - I)A_{\text{geo}}}{2\nu C_A}$$

[6]

Linear regression analysis (Table III) of Tafel plots (Fig. 5) of pristine and doped Ti$_4$O$_7$ disk electrodes in 0.5 M H$_2$SO$_4$ suggests that V- and Cr-doping have a minimal influence on the Tafel behavior or Ti$_3$O$_5$. Assuming that the OER is the exclusive electrochemical reaction at the electrode in 0.5 M H$_2$SO$_4$, Ti$_4$O$_7$ is a poor electrocatalyst for the reaction, exhibiting sluggish kinetics as described by a large Tafel slope ($b$) of 400 ± 10 mV dec$^{-1}$ and a small exchange current density ($j_0$) of 10$^{-3.5±0.4}$ mA cm$^{-2}$geo or 10$^{-4.7±0.3}$ mA cm$^{-2}$ECSA. This exchange current density is comparable with an estimated value for porous Ti$_4$O$_7$ electrodes of 10$^{-5.1}$ mA cm$^{-2}$ECSA based on a reported exchange current density of 3.95 × 10$^{-3}$ mA cm$^{-2}$geo and a surface roughness of 500 ($-\log_{10}(j_0/j_\text{c})$) in 0.5 M Na$_2$SO$_4$ (25 °C). This Tafel behavior is observed by pristine Ti$_4$O$_7$ up to as high a current density of 100 mA cm$^{-2}$geo, after which the Tafel slope increases abruptly. This abrupt change in the Tafel slope at high current density is attributed to the loss of ECSA due to blockage of the electrode surface by considerable evolution of gas. Similar Tafel behavior is also exhibited by V- and Cr-doped Ti$_4$O$_7$ with small differences in the Tafel slope and the exchange current density for Cr- and V-doped samples, respectively. Fe-doped Ti$_4$O$_7$, however, shows considerably different behavior with significantly different Tafel parameters. Furthermore, the Tafel slope of Fe-doped samples increases abruptly at current densities as low as 20 mA cm$^{-2}$geo, rendering it unsuitable for ALT at high current densities (vide infra) given the impractically-large overpotentials required.

V-doping improves anodic stability.—V-doped Ti$_4$O$_7$ disk electrodes are more anodically stable as demonstrated by ALT. Selected chronopotentiograms (CPs) of pristine and doped Ti$_4$O$_7$ disks in 0.5 M H$_2$SO$_4$ (Fig 6) illustrate typical behaviors. Generally, after a short period of conditioning, the electrode potential is ~3–4 V (vs NHE), consistent with the overpotential predicted by parameters obtained by fitting Tafel plots (vide supra) given the equilibrium potential of 1.2 V (vs NHE). This electrode potential is relatively stable for a period of time, after which the electrode potential increases, suggesting an increase in the resistance of the electrode, which is supported by EIS (vide infra). A mechanism for passivation of Ti$_4$O$_7$ is its electrochemical oxidation forming TiO$_2$ (Eq. 7),11–13 which is electrically insulating.
The electrode potential continues to increase at an increasing rate until the electrode "fails", indicated by an asymptotic increase to large potential values. From statistical analysis of CPs generated by ALT (Table IV), it can be seen that the TTF for V-doped Ti$_4$O$_7$ is 2.57 times that of pristine Ti$_4$O$_7$ disk electrodes, which have a TTF of 101.78±0.06 h. Similar to the improved anodic stability of Ce-doped Ti$_4$O$_7$ sintered disk electrodes, which provides a 20% improvement in the TTF, it is speculated that V-doping may stabilize oxygen vacancies. Cr-doping, however, is shown to have a 40% reduction in its TTF relative to the pristine material. The influence of Fe-doping on anodic stability was not investigated due to its high overpotential at 100 mA cm$^{-2}$geo and is therefore unclear. However, were these tests conducted at a lower current density such as 20 mA cm$^{-2}$geo, one would predict a TTF for V-doped Ti$_4$O$_7$ disk electrodes in excess of 3 months (Eq. 2, $t = 1.7$), illustrating the challenge in evaluating the stability of Fe-doped Ti$_4$O$_7$ disk electrodes using ALT with lower current densities.

Nyquist (Fig. 7) and Bode plot analysis (Fig. S3) of impedance data obtained by EIS of pristine, V-, and Cr-doped Ti$_4$O$_7$ disk electrodes at the beginning and end of life (BOL and EOL, respectively) reveal insights into the mechanism of passivation. At the BOL, there appears to be two time constants in all impedance data as indicated by the two semicircles in the Nyquist plot and the phase ($\phi$) being non-zero at frequencies on the order of 10$^{-1}$–10$^{0}$ and 10$^{2}$–10$^{3}$ Hz in the Bode plots. As XPS analysis suggests that there is a thin film of TiO$_2$ on the surface, an equivalent electrical circuit (EEC) for this system could be a Voigt-type electrical circuit (Fig. S4), consisting of a resistor then two Voigt elements in series, a Voigt element being a parallel resistor and capacitor unit. In such an EEC, the resistor expresses the solution resistance, one Voigt element describes the contribution of the thin film of TiO$_2$ to the circuit, and the other accounts for the charge-transfer resistance and double-layer capacitance. Near the EOL, the pristine Ti$_4$O$_7$ disk electrode still appears to have two time constants, though the magnitude of the impedance increases, suggesting an increase in the thin film and charge-transfer resistances. This could be explained by the growth in thickness of the thin film of TiO$_2$ and loss of ECSA as the electrode passivates. Ebonex$^\text{®}$ and Ti$_4$O$_7$ electrodes are shown to oxidize upon extended anodic treatment as evidenced by X-ray diffractometry, forming Ti$_6$O$_{11}$—a Magnéli phase titanium oxide whose electrical conductivity is ∼500 times lower than that of Ti$_4$O$_7$. The doped Ti$_4$O$_7$ disk electrodes at the EOL also have increased impedance, but only one time constant, suggesting that the EEC has converged into a simple parallel resistor and capacitor followed by a resistor in series circuit. As a result, the charge-transfer resistance increases, suggesting that the conditions of the ALT has sufficiently inhibited the electrocatalytic activity of these electrodes for the OER.

![Figure 5](image-url)  
**Figure 5.** Selected Tafel plots of pristine and doped Ti$_4$O$_7$ disk electrodes (2,000 RPM) in 0.5 M H$_2$SO$_4$ (pH 0.4, 22 °C) for the oxygen evolution reaction.

\[
\text{Ti}_4\text{O}_7 + \text{H}_2\text{O} \rightarrow 4\text{TiO}_2 + 2\text{H}^+ + 2\text{e}^-.
\]  

The electrode potential continues to increase at an increasing rate until the electrode “fails”, indicated by an asymptotic increase to large potential values. From statistical analysis of CPs generated by ALT (Table IV), it can be seen that the TTF for V-doped Ti$_4$O$_7$ is 2.57 times that of pristine Ti$_4$O$_7$ disk electrodes, which have a TTF of 101.78±0.06 h. Similar to the improved anodic stability of Ce-doped Ti$_4$O$_7$ sintered disk electrodes, which provides a 20% improvement in the TTF, it is speculated that V-doping may stabilize oxygen vacancies. Cr-doping, however, is shown to have a 40% reduction in its TTF relative to the pristine material. The influence of Fe-doping on anodic stability was not investigated due to its high overpotential at 100 mA cm$^{-2}$geo and is therefore unclear. However, were these tests conducted at a lower current density such as 20 mA cm$^{-2}$geo, one would predict a TTF for V-doped Ti$_4$O$_7$ disk electrodes in excess of 3 months (Eq. 2, $t = 1.7$), illustrating the challenge in evaluating the stability of Fe-doped Ti$_4$O$_7$ disk electrodes using ALT with lower current densities.

Nyquist (Fig. 7) and Bode plot analysis (Fig. S3) of impedance data obtained by EIS of pristine, V-, and Cr-doped Ti$_4$O$_7$ disk electrodes at the beginning and end of life (BOL and EOL, respectively) reveal insights into the mechanism of passivation. At the BOL, there appears to be two time constants in all impedance data as indicated by the two semicircles in the Nyquist plot and the phase ($\phi$) being non-zero at frequencies on the order of 10$^{-1}$–10$^{0}$ and 10$^{2}$–10$^{3}$ Hz in the Bode plots. As XPS analysis suggests that there is a thin film of TiO$_2$ on the surface, an equivalent electrical circuit (EEC) for this system could be a Voigt-type electrical circuit (Fig. S4), consisting of a resistor then two Voigt elements in series, a Voigt element being a parallel resistor and capacitor unit. In such an EEC, the resistor expresses the solution resistance, one Voigt element describes the contribution of the thin film of TiO$_2$ to the circuit, and the other accounts for the charge-transfer resistance and double-layer capacitance. Near the EOL, the pristine Ti$_4$O$_7$ disk electrode still appears to have two time constants, though the magnitude of the impedance increases, suggesting an increase in the thin film and charge-transfer resistances. This could be explained by the growth in thickness of the thin film of TiO$_2$ and loss of ECSA as the electrode passivates. Ebonex$^\text{®}$ and Ti$_4$O$_7$ electrodes are shown to oxidize upon extended anodic treatment as evidenced by X-ray diffractometry, forming Ti$_6$O$_{11}$—a Magnéli phase titanium oxide whose electrical conductivity is ∼500 times lower than that of Ti$_4$O$_7$. The doped Ti$_4$O$_7$ disk electrodes at the EOL also have increased impedance, but only one time constant, suggesting that the EEC has converged into a simple parallel resistor and capacitor followed by a resistor in series circuit. As a result, the charge-transfer resistance increases, suggesting that the conditions of the ALT has sufficiently inhibited the electrocatalytic activity of these electrodes for the OER. It is unclear, however, whether this is due to

### Table III. Summary of statistical analysis (3 observations, 5% significance level) of fitted Tafel parameters$^a$ of pristine and doped Ti$_4$O$_7$ disk electrodes (2,000 RPM) in 0.5 M H$_2$SO$_4$ (0.4 pH, 22 °C).

| Electrode | $b$ (mV dec$^{-1}$) | $-\log_{10}(j_0$/mA cm$^{-2}$) | $-\log_{10}(j_0$/mA cm$^{2}$ECSA$^{-2}$) |
|-----------|---------------------|-----------------------------|---------------------------------|
| Pristine  | 400 ± 10            | 3.5 ± 0.4                   | 4.7 ± 0.5                      |
| V-doped   | 460 ± 50            | 2.5 ± 0.5                   | 3.5 ± 0.6                      |
| Cr-doped  | 350 ± 20            | 3.4 ± 0.3                   | 4.5 ± 0.4                      |
| Fe-doped  | 860 ± 330           | 1.0 ± 0.5                   | 2.1 ± 0.6                      |

$^a$ i.e., Tafel slope, $b$, and exchange current density, $j_0$, the latter normalized for both geometric and electrochemically-active surface areas (subscripts “geo” and “ECSA”, respectively).

![Figure 6](image-url)  
**Figure 6.** Selected chronopotentiograms (100 mA cm$^{-2}$geo) of pristine and doped Ti$_4$O$_7$ disk electrodes (2,000 RPM) in 0.5 M H$_2$SO$_4$ (pH 0.4, 22 °C).
Table IV. Summary of statistical analysis (3 observations, 5% significance level) of time-to-failures (TTFs, 100 mA cm\(^{-2}\)) of pristine and doped Ti\(_4\)O\(_7\) disk electrodes in 0.5 M H\(_2\)SO\(_4\) (pH 0.4, 22 °C).

| Electrode   | log\(_{10}\) (TTF/hours) |
|------------|--------------------------|
| Pristine   | 1.78 ± 0.06              |
| V-doped    | 2.19 ± 0.07              |
| Cr-doped   | 1.56 ± 0.09              |

Figure 7. Nyquist plots (100 ± 1 mA cm\(^{-2}\)) of pristine and doped Ti\(_4\)O\(_7\) disk electrodes (2,000 RPM) in 0.5 M H\(_2\)SO\(_4\) (pH 0.4, 22 °C) at the beginning (BOL, full circles, *) and near the end of life (EOL, open circles, O) during accelerated life testing.

Conclusions

Ti\(_4\)O\(_7\)\(_{2n-1}\)-based materials are of growing importance to aqueous electrochemical technologies and developing strategies to tailor their relevant physicochemical properties are needed to address any material shortcomings. As this work demonstrates, V-doping significantly improves the anodic stability of Ti\(_4\)O\(_7\), greatly increasing its time-to-failure as suggested by electrochemical accelerated life testing. Vanadium-doped materials also exhibit improved electrical conductivity, which is conducive to the development of effective high-surface area electrodes such as reactive electrochemical membranes. The use of high-surface area electrodes would allow for high geometric current densities while maintaining relatively modest current densities normalized for ECSA, increasing the time-to-failure. While the investigated doping level was limited to 2 at%, this composition was not optimized. Therefore, studies exploring the influence of dopant type, doping level, and co-doping on oxidation stability as well as other properties relevant to electrodes such as electrical conductivity and electrochemical behavior will develop a richer understanding of the interplay between doping and electrode characteristics. Finally, the use of V-doped Ti\(_4\)O\(_7\)\(_{2n-1}\)-based materials looks promising for use in aqueous electrochemical technologies such as fuel cells, batteries, and devices for the electrochemical treatment of water.

Acknowledgments

The authors acknowledge technical assistance from H. Eunike of the Electron Microscopy Lab at the University of British Columbia (UBC) with SEM and EDX, and M. Wang of 4D Labs at Simon Fraser University with XPS. The authors acknowledge funding in support of research from the Natural Sciences and Engineering Research Council of Canada (NSERC) Discovery Grant Program. J.T. English acknowledges funding in support of his graduate studies from the NSERC Canada Graduate Scholarships Program, the NSERC Collaborative Research and Training Experience Program in Nanomaterials Science and Technology, the Killam Doctoral Scholarship, the 4 Year Fellowship at UBC, and the John Tiedje Fellowship in Clean Energy and Greenhouse Gas Mitigation.

ORCID

Joseph T. English https://orcid.org/0000-0002-1614-8777

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