



Enhanced Power Generation in Lithium-Doped Tantalum Oxide Hydroelectric Cell

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Abstract

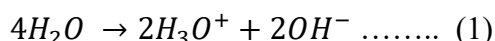
The global green energy demand has led to the development of the Hydroelectric cell (HEC). It is a device that generates electricity through water dissociation on oxygen deficient nanoporous metal oxide surfaces. The dissociation of water produces hydronium and hydroxide ions which undergo electrochemical reactions at the electrodes, generating emf and current. This study investigates the performance of pristine and lithium doped tantalum oxide based HEC. Experimental results demonstrate that doping Ta₂O₅ with lithium significantly enhances current and power output compared to the undoped sample. The pure Ta₂O₅ based HEC produced a short circuit current (I_{sc}) of 0.3 mA and an open circuit voltage (V_{oc}) of 1.23 V compared to the Li doped Ta₂O₅ HEC. It exhibited a substantially higher short circuit current of 2.4 mA and an open circuit voltage of 0.966 V. The doped sample based HEC delivered a power output of ~ 0.25 mW in comparison to the undoped sample which delivered a maximum power output of ~ 0.074 mW. Electrochemical impedance spectroscopy (EIS) revealed that lithium doping reduced the charge transfer resistance and promoted ionic conduction in the doped sample, as evidenced by the extended Warburg diffusion tail in the Nyquist plot. Lithium doping facilitated more efficient water dissociation and ion transport in the sample. The increase power output in the Li doped sample has been attributed to the increased oxygen vacancies, surface defects and nano porosity induced by lithium.

Keywords: Ta₂O₅, Water splitting, Oxygen vacancies, Green energy, HEC.

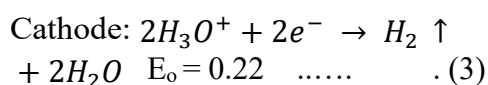
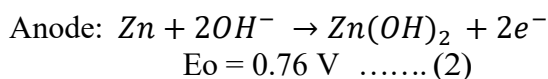
1. Introduction: The fast depletion of fossil fuels and the current climate change scenario have created an urgent need for clean and sustainable energy technologies.

Among emerging technologies, the Hydroelectric cell (HEC) has attracted considerable attention as a green energy device. The nano porous, oxygen deficient

surface of the HEC material spontaneously dissociates water molecules at room temperature without using any acid/alkali or photons [1–4]. Unlike conventional fuel cells or electrolyzers, HECs exploit the simple oxides materials to spontaneously dissociate water molecules on the material surface. Hence HEC offers a pathway for low cost and catalyst free energy generation. The basic principle involves the dissociation of water molecules into H_3O^+ and OH^- ions on the defective surface of the material.



The trapped protons in the nanopores generate strong electric fields of the order of 10^4 V/cm which is sufficient enough to dissociate water molecules in the physisorbed layers over the material surface. The hydroxide ions migrate towards zinc electrode where they are oxidized to form zinc hydroxide. On the other hand, the dissociated hydronium ions in the physisorbed layers migrate towards the silver cathode where they are reduced to hydrogen gas. These electrochemical reactions at electrodes establishes a potential difference across the cell as depicted in the equations below [5–7].



Thus, a Hydroelectric cell delivers an EMF of 0.98 V (0.76V + 0.22 V). The current

generation in Hydroelectric cell critically depends on the defect concentration, importantly the number of oxygen vacancies and the ionic conductivity of the oxide material [8]. Consequently, the enhancement in the defect density and porosity in the oxide material under study directly affect the performance of the Hydroelectric cell with the improved power density.

Tantalum oxide (Ta_2O_5) is a wide bandgap (3.8-4.5 eV) transition metal oxide with excellent chemical stability, environmental inertness and prominent ionic conductivity [9,10]. The open crystal framework and tendency to accommodate dopants in the lattice interstitials make it a potential candidate for water splitting and hence energy production as Hydroelectric cell. However, the pure tantalum oxide is known to have low defect density which limits the dissociation of water on its surface. Lithium doping has been widely reported in metal oxide systems to tailor defect chemistry of the lattice. In case of Ta_2O_5 the substitution of Li^+ for Ta^{5+} creates charge imbalance in the lattice. This charge imbalance is then compensated by the formation of oxygen vacancies. The smaller ionic radius of Li^+ introduces lattice strain that is supposed to increase porosity of the sample and hence the surface area [11]. These structural and chemical modifications are expected to enhance the performance of tantalum oxide based HECs.

Despite the extensive literature on doped metal oxide based HECs, like zinc oxide [12,13], titanium oxide [4], iron oxide [14,15] nickel ferrite [16,17] etc., tantalum oxide based HECs have not been reported so far. The present work addresses this gap by the study of pure and lithium doped tantalum oxide. The hydroelectric cells from both doped and undoped tantalum oxides were fabricated. A comprehensive electrochemical characterization, including voltage-current polarization curves and

electrochemical impedance spectroscopy was performed. The superior performance of the doped sample has been systematically linked to enhanced oxygen vacancy, increased nano porosity and improved ionic conductivity of the lattice arising from lithium doping.

2. Materials and Methods: Synthesis of pure and Li doped tantalum oxide: Pure tantalum oxide was synthesized by the solid-state method. For this Ta_2O_5 was purchased from Thermo Fischer Chemicals (99.9 % purity). 2 g of Ta_2O_5 was hand grinded in a pestle and mortar using acetone solvent, for 30 minutes. Another sample was prepared with 40 wt% lithium doping in Ta_2O_5 . For this, 1.98 g of Li_2CO_3 (Speck pure, 99 % purity) was added to 1.2 g of Ta_2O_5 and it was also hand grinded in a similar manner. After grinding, both samples were presintered at 850 °C for 6 hours. After cooling, the samples were again grinded and pressed in the shape of circular pellets having diameter of 1.2 cm, using a hydraulic press. These pellets were then sintered at 950 °C for 4 hours, and later used for fabricating hydroelectric cells.

2.1 Hydroelectric Cell Fabrication: Hydroelectric cells were assembled by adding a zinc sheet at one face of the pellet as anode, while at the other face silver was comb patterned as cathode. The pristine tantalum oxide sample was labelled as PTO and the lithium doped tantalum oxide

contacts were made at both electrodes for measuring the device's power response.

2.1 Electrochemical Characterization: Voltage-current (V-I) characteristics were recorded using a potentiostat (Keithley 2430 1 kW pulse source meter) by varying the load across the HECs and measuring the voltage drop with increasing cell current. Power ($P = V \times I$) was computed from the measured V-I data. Electrochemical impedance spectroscopy (EIS) was performed using a Wayne-Kerr Impedance Analyzer 6500B over a frequency range of 20 Hz to 120MHz with an AC perturbation amplitude of 25 mV. Nyquist plots were analyzed to extract the series resistance (R_s), charge transfer resistance (R_{ct}) and Warburg diffusion (W).

3. Results and Discussion:

3.1 V-I Polarization Characteristics

Figure 1 represents the V-I polarization curves and corresponding power curves for both pure and doped tantalum oxide based Hydroelectric cells. The pure Ta_2O_5 cell exhibited an open circuit potential (V_{oc}) of 1.23 V and a short circuit current (I_{sc}) of ~0.30 mA. The cell delivered a maximum power output (P_{max}) of approximately 0.074 mW. In contrast, the lithium doped cell delivered an open circuit potential (V_{oc}) of 0.97 V and a substantially increased short circuit current of I_{sc} of ~2.4 mA. The doped cell achieved a P_{max} of approximately 0.25

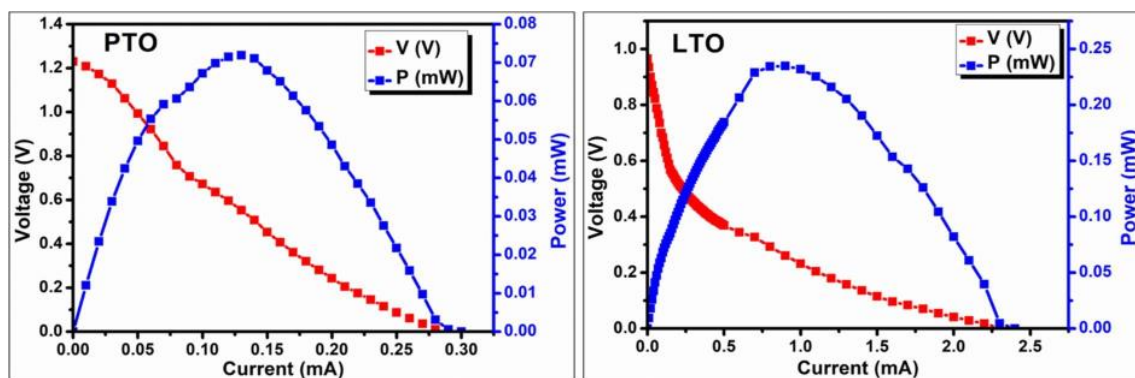


Figure 1: V-I (red) and power-current (blue) characteristics of (left) pure tantalum oxide and (right) lithium doped tantalum oxide based Hydroelectric cells

powder was labelled as LTO. Electrical

mW. Approximately a 3.4 fold increase in

peak power output was obtained upon lithium doping.

The V-I curves for both samples showed the Hydroelectric cell characteristic, reflecting the water dissociation on material surface and electrochemical reactions at the electrode interfaces [18]. The significantly

HECs in the range of 20-120 MHz. The EIS spectra provided a critical insight into the resistance and ionic transport properties of both the samples. The spectra showed significant difference between their electrochemical performances.

The Nyquist plot of pure tantalum oxide

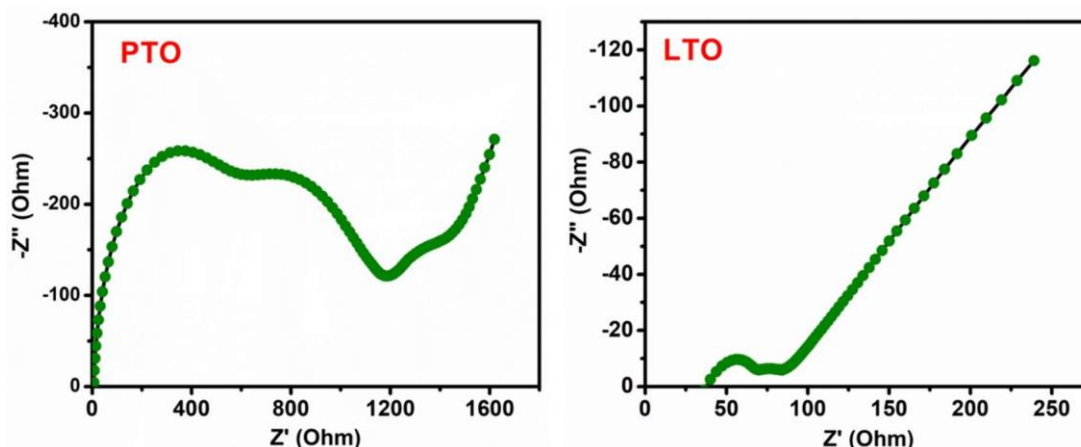


Figure 2: Nyquist plots (EIS) of pure tantalum oxide (at left) and lithium doped tantalum oxide (at right) based Hydroelectric cells, frequency range: 20 Hz to 200 MHz.

higher short circuit current in lithium doped tantalum oxide is indicative of a greatly enhanced water dissociation and ion transport in the material. The slight reduction in open circuit potential of the doped sample in comparison to the pure (~ 0.97 V vs. 1.23 V) was compensated by the gain in current, resulting in the effective improvement in power output. Table 1 summarizes the key performance parameters obtained from both HECs.

Table 1: Current, voltage and power output of pure and lithium doped tantalum oxide based Hydroelectric cells

	Current (mA)	Voltage (V)	Power (mW)
Pure Ta_2O_5	0.3	1.23	0.369
Li doped Ta_2O_5	2.4	0.966	2.318

3.2 Electrochemical Impedance Spectroscopy

Figure 2 represents the Nyquist plots obtained for pure and doped samples based

displayed a broad, depressed semicircular arc spanning approximately 0-1600 Ω along the real impedance axis (Z'), with a peak imaginary impedance ($-Z''$) of about 250 Ω . The shape showed by the pure sample based HEC is characteristic of overlapping RC time constants associated with grain, grain boundary resistance and charge transfer resistance dielectric relaxation within the oxide matrix. The high impedance magnitude at low frequency (~ 1600 Ω) confirmed that the undoped sample offers significant resistance to both electronic and ionic transport. In contrast, the Nyquist spectrum of lithium doped tantalum oxide was dramatically compressed along the Z' axis (0-250 Ω), indicating a significant reduction in total impedance. The small, high frequency semicircle ($Z' \approx 40-90$ Ω) represents grain/grain-boundary resistance and charge transfer processes at the electrode electrolyte interface. The prominent, near linear, low frequency tail extending steeply is representative of Warburg diffusion [19,20]. The Warburg element arises from semi-infinite diffusion of hydronium (H_3O^+) and hydroxide (OH^-)

ions through the nanoporous oxide. Its pronounced character in the doped sample is a direct consequence of the enhanced porosity and interconnected pore network introduced by lithium doping. The steep Warburg tail is consistent with diffusion controlled ion transport within a confined porous structure, indicative of capacitive behavior at the electrode electrolyte interface [21]. The reduced R_s and R_{ct} values in the doped sample, extracted from the high frequency intercept and semicircle diameter respectively, confirmed that lithium doping substantially reduced both bulk resistance and interfacial charge transfer barriers. The lower resistance facilitated faster and more efficient migration of dissociated hydronium and hydroxide ions through the sample pellet leading to 8 fold increase in short circuit current and the ~ 3.4 fold increase in maximum power as observed in the V-I measurements.

Oxygen vacancies are the primary active sites for water adsorption and its chemi-dissociation on material surface [1,22]. The substitution of Li^+ on a Ta^{5+} site introduced negative effective charges that were compensated by the formation of oxygen vacancies. These defect sites strongly adsorbed water molecules and promoted its dissociation into H_3O^+ and OH^- . The higher oxygen vacancy in the doped sample, therefore directly amplified the rate of water splitting and hence, increasing the current generation. Surface defects, including grain boundaries and under coordinated surface Ta sites, introduced additional centers for water adsorption. The nanoporosity of the oxide material is a further critical parameter governing HEC performance [23,24]. During the calcination of the Li-doped precursor, the decomposition of Li_2CO_3 forms Li_2O and CO_2 gas is released that creates a network of nanopores within the Ta_2O_5 lattice. This nanoporous structure dramatically increased the specific surface area available for water interaction, while simultaneously providing ionic diffusion

pathways responsible for the extended Warburg tail in the doped Nyquist spectrum. The combination of higher surface area, greater oxygen vacancy density, and improved ionic conductivity collectively amplifies the overall HEC output in LTO.

4. Conclusions:

This study has demonstrated that lithium doping of tantalum oxide markedly enhances the performance of hydroelectric cells. The LTO HEC delivered a short-circuit current of 2.4 mA and a peak power of ~ 0.25 mW, representing improvements of approximately 8-fold and 3.4-fold respectively over the pristine PTO device. EIS analysis confirmed that lithium doping reduces bulk and charge-transfer resistance and promotes extensive Warburg type ionic diffusion, indicative of a highly porous, ionically conducting oxide matrix. The enhanced performance of LTO is attributed to increased oxygen vacancy defects that act as active sites for water dissociation, and also facilitating faster interfacial charge transfer. The enhanced nano porosity provided a large surface area and efficient ion transport pathways for H_3O^+ and OH^- ion migration. These findings establish Li doped Ta_2O_5 as a promising material for improving water-splitting in hydroelectric cells.

Acknowledgement

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Conflict of Interest

There is

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