

Metal Oxide Based Hydroelectric Cell for Electricity Generation by Water Molecule

Dissociation without Electrolyte/Acid

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Surface Morphology of metal Oxide HECs

The grain size distribution as well as mesopore formation has been estimated by SEM images. Smallest average grain size ~ 65 nm with nanopores of average 40 nm size has been observed in MgO, whereas increased grain size formation is found in SnO₂, TiO₂, ZnO, Al₂O₃ and SiO₂ respectively. Agglomeration of small grains with average grain size distribution ~ 200 nm has been found in SnO₂ while grain size ~135 nm is observed in TiO₂. The pore size distribution ~ 150 nm with some large open pores has been recorded in SnO₂ and small mesopores ~ 125nm are observed in TiO₂. Uniform grain size ~ 340 nm has been observed in ZnO along with homogeneous mesopore formation of the order of 150 nm. On the other hand, large island like non uniform grain formation has been detected in Al₂O₃. Bimodal grain size distribution of average grain size ~ 400 nm with large open pores and interstices have been recorded in Al₂O₃. Non uniform grain size distribution with appearance of large and small clusters are found in SiO₂. The average grain size has been calculated ~ 500 nm and pores are in ~ 280 nm size in SiO₂.

Supplementary Table S1: Calculation of chemidissociated ions at the surface of metal oxides by inceptive current measurements:

Introducing few drops of water molecules results into initial chemidissociation of water molecules at defect and vacancy sites present at metal oxide surface. The surface current generated due to flow H^+ / OH^- ions between two silver electrodes at surface was measured by two probe method. Initial number of chemidissociated ions were calculated by the formula $I = ne/2$ where I is the initial current produced due to water dissociation, n is the no. of ions generated and e is electric charge. The calculated value of number of chemidissociated ions has been listed in Table S1:

Name of metal oxide	Surface current density ($\mu A/cm^2$)	No. of chemidissociated ions
SnO₂	0.790	9.8E12
Al₂O₃	0.587	7.2E12
ZnO	0.620	7.7E12
TiO₂	0.142	1.7E12
MgO	0.119	1.48E12
SiO₂	0.130	2.1E12

Supplementary Table S2: Change of pH of DI water (20 ml) with time by adding fixed amount 1gm of metal oxides.

For each oxide, 1 gm pellet was poured in 20 ml deionized water and subsequent change in pH was monitored for fixed time 60 sec as depicted in Table1. It has been observed that SnO₂ enhances the pH of water maximum from 6.5 to 9.37 compared to other oxides due to highest rate of dissociation of water molecules. The least change in pH has been observed for TiO₂ ~ 6.5 to 6.62 due to slowest rate of water dissociation by TiO₂.

Sample	SnO ₂	Al ₂ O ₃	ZnO	TiO ₂	MgO	SiO ₂
Change in pH (DI water)	6.5-9.37	6.5 -8.41	6.5-7.00	6.5-6.62	6.5 -7.33	6.5-7.00
Time (Seconds)	60	60	60	60	60	60

Supplementary Table S3: Calculated parameter for V/I polarization by non-linear curve fitting

$$\text{Equation: } V_{out} = E_0 - [A \ln\left(\frac{I}{I_0}\right) - IR - m \ln(1 - \frac{I}{I_l})]$$

where E_0 is reversible cell potential, A is Tafel slope, I_0 is exchange current density, R is ohmic resistance for ion flow, m is constant and I_l is limiting current density

Parameters	SnO ₂	Al ₂ O ₃	ZnO	TiO ₂	MgO	SiO ₂
E_0	0.76	0.99	0.91	0.96	0.99	1.00
A	0.051	0.051	0.013	0.033	0.015	0.017
I_0	1.77E-6	5.13E-7	6.00E-8	8.50E-8	1.47E-9	3.1E-10
R	19.63	943.20	335.07	284.85	1275.76	1075.9
M	0.079	0.038	0.610	0.017	0.344	0.636
I_l	25.08	7.20	6.42	2.37	1.52	1.96

Supplementary Table S4: BET Surface area

The pore size distribution and specific surface area of metal oxide pellets has been calculated by BET surface area analysis. Specific parameters including pore size, pore volume and specific surface area are given in Table S2(a) and Table S2(b):

Table-S4 (a) Pore Size distribution

Name (Metal Oxide)	Total pore volume at P/Po = 0.99435	Pore Diameter (nm)
SnO₂	8.564e-03 cc/g for pores smaller than 201.2 nm (Diameter)	DA method = 2.380 nm BJH method = 3.459 nm
Al₂O₃	1.640e-02 cc/g for pores smaller than 372.8 nm (Diameter)	DA method = 2.420 nm BJH method = 6.603 nm
ZnO	2.01e-03 cc/g for pores smaller than 300 nm (Diameter)	DA method = 2.480 nm BJH method = 3.442
TiO₂	1.560e-02 cc/g for pores smaller than 263.4 nm (Diameter)	DA method = 3.068 nm BJH method = 3.073 nm
MgO	4.533e-02 cc/g for pores smaller than 100 nm (Diameter)	DA method = 3.769 nm BJH method = 3.107 nm
SiO₂	5.114e-03 cc/g for pores smaller than 252.6 nm (Diameter)	DA method = 5.670 nm BJH method = 3.064 nm

Table-S4(b) Surface Area Data

Name (Metal Oxide)	BJH Method Cumulative Adsorption Surface Area (m²/g)	Multipoint BET (m²/g)	BJH Method Cumulative Desorption Surface Area (m²/g)
SnO₂	2.531	4.978	2.337

Al₂O₃	5.946	10.968	4.900
ZnO	1.056	1.699	0.754
TiO₂	4.820	11.182	5.205
MgO	21.945	37.450	21.457
SiO₂	1.365	3.279	1.349

Supplementary Fig. S1 Dielectric loss v/s frequency plot of metal oxide HEC's in dry state:

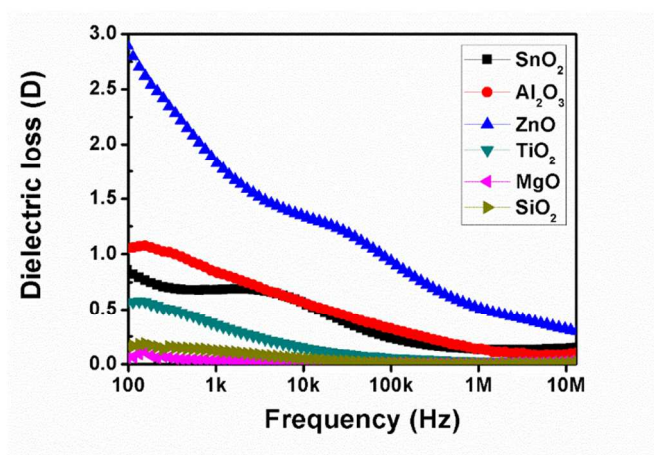


Fig S1 Frequency dependence of dielectric loss of metal oxide HECs without any water (in dry state) where no response of grain boundary relaxation is visible.

Supplementary Fig. S2 Analytical complex impedance ($-Z''$ v/s Z') fitting of wet metal oxide HECs with equivalent circuit

In order to identify individual resistance contribution from electrode/material/interface to the charge flow in HEC, equivalent circuit analysis has been performed by using EIS analyzer under wet condition of cells. The equivalent circuit is shown in Fig.S2, where L represents inductance and R resistance of metallic elements of cell at very high frequencies. R_{ct} corresponds to charge transfer resistance of electrodes and R_b is accounted for bulk resistance of oxide material and it acts during cycling at the surface of anode. Constant phase element (CPE) has

been used in place of capacitor in order to compensate for non-ideal behavior of electrode due to surface roughness or porosity. Diffusion of ions is represented by a Warburg element (W).

Fig.S3 represents the analytical plots of wet metal oxide cells fitted with the equivalent circuit.

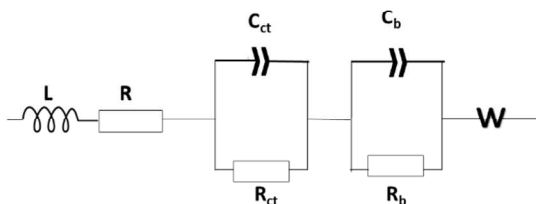


Fig.S2 Equivalent circuit used for fitting the impedance data in wet metal oxide HECs.

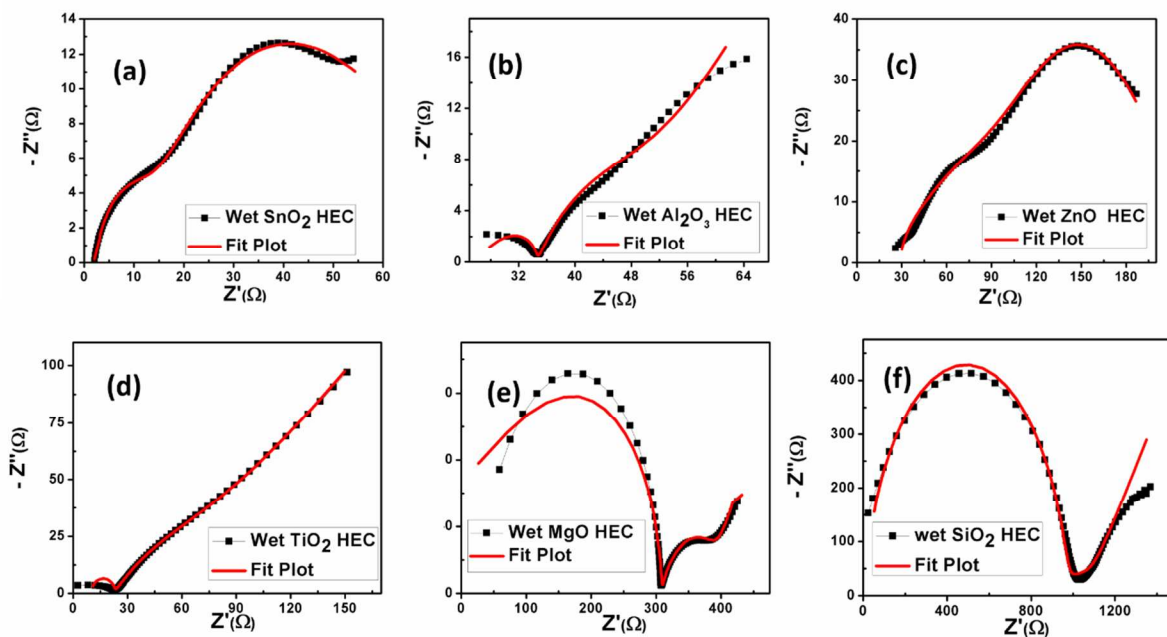


Fig. S3 Analytical complex impedance ($-Z''$ v/s Z') plots of wet metal oxide HECs fitted with equivalent circuit.