

ESI Fig. 1 Equivalent circuit diagram for fitting the impedance data. R_s describes the series resistance of the transparent conductive oxide, R_{tr} the transport resistance of the porous semiconductor, the RC element consisting of C_{μ} and R_{rec} the charge transfer at the semiconductor/electrolyte interface, Z_d a Warburg element to describe the charge transfer in the electrolyte and the RC element R_{Pt} and C_{Pt} to describe the charge transfer at the electrolyte/platinum interface.



ESI Fig. 2 IV-curves under AM 1.5 conditions of DSC of porous ZnO electrodeposited from a perchlorate-containing electrolyte on an electrodeposited blocking layer from a perchlorate solution (- \triangle -) or on a sputter-deposited blocking-layer (- \bigcirc -) and of porous ZnO electrodeposited from a chloride-containing electrolyte on a sputter-deposited blocking layer (- \bigcirc -). For comparison an IV-curve of established DSC of porous ZnO electrodeposited from a chloride-containing electrolyte on an electrodeposited blocking layer from a chloride solution is also shown (- ∇ -).



ESI Fig. 3 Internal voltage plotted against the density of states in DSC of porous ZnO electrodeposited from a perchlorate-containing electrolyte on an electrodeposited blocking layer from a perchlorate solution (- • -) or on a sputter-deposited blocking-layer (- • -) and of porous ZnO electrodeposited from a chloride-containing electrolyte on a sputter-deposited blocking layer (- • -).



 $\label{eq:photoenergy/eV} \mbox{ESI Fig. 4} Tauc-Plot of a ZnO(Cl^-) and ZnO(ClO_4^-) sample to determine the optical band gap of both different ZnO samples$

Sample	C / at. %	O / at. %	Cl / at. %	Zn / at. %
ZnO(Cl ⁻)	17.74±0.42	50.76±1.70	0.16±0.02	31.44±1.96
ZnO(ClO ₄ -)	14.64±2.06	59.92±6.23	0.16±0.06	21.91±5.00

ESI Tab. 1 Mean values of atomic percentages of film constituents obtained from energy-dispersive X-ray analysis (EDX) of at least two samples. It should be noted that EDX does not allow to quantitatively discuss changes in the range below 1 at. %.