

Electrochemical reduction of O₂ in 1-butyl-1-methylpyrrolidinium bis(trifluoromethane sulfonyl)imide ionic liquid containing Zn²⁺ cations: towards the deposition of non-polar oriented ZnO nanocrystalline films

Eneko Azaceta^a, Rebeca Marcilla^a, David Mecerreyes^a, Mariana Ungureanu^b, Apurba Dev^c, Tobias Voss^c, Sébastien Fantini^d, Hans-Jurgen Grande^a, Germán Cabañero^a, Ramón Tena-Zaera^{a,}*

^aNew Materials Department, CIDETEC, Centre for Electrochemical Technologies, Parque Tecnológico de San Sebastián, Paseo Miramón 196, Donostia-San Sebastián 20009, Spain

^bCIC BIOMAGUNE, Parque Tecnológico de San Sebastián, Paseo Miramón 182 C, Donostia-San Sebastián 20009, Spain

^cInstitute of Solid State Physics, University of Bremen, P.O. Box 330440, 28334 BREMEN, Germany

^dSolvionic, Chemin de la Loge, Toulouse 31078, France

Supplementary Information

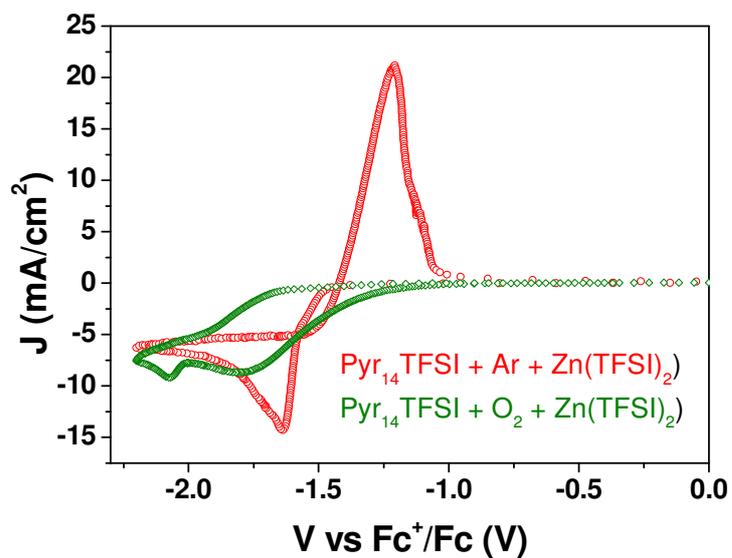


Figure S1. Voltammograms of PYR₁₄TFSI, Zn(TFSI)₂ bubbled with Ar (○, red) and O₂ (◇, green). In other words, the latter corresponds to the full electrolyte (PYR₁₄TFSI, Zn(TFSI)₂ + O₂) used for the ZnO electrodepositions. The concentration of Zn(TFSI)₂ is 5x10⁻² M in both cases.

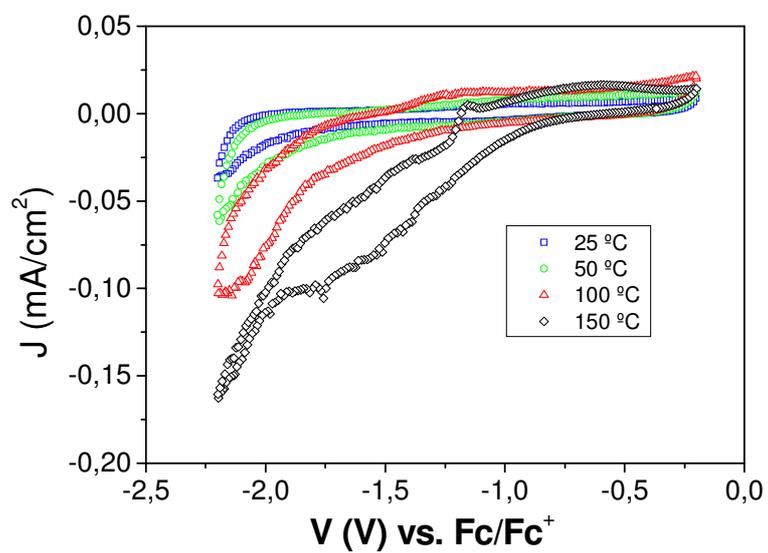


Figure S2. Cyclic voltammograms of Argon purged Pyr₁₄TFSI at 25 °C (□, blue), 50 °C (○, green), 100 °C (Δ, red) and 150 °C (◇, black).

Table S1. Atomic concentration of each element obtained from the depth profiling XPS analysis for samples electrodeposited at different temperatures: 75, 100 and 150 °C.

		Energy (eV)	No Ar etching	Ar etching					
				1 min	5 min	10 min	15 min	20 min	30 min
Deposited at 75 °C	C 1s	285.0	26.6%	13.5%	10.0%	9.0%	7.2%	9%	7%
	Zn 1s	1022.5	27.8%	43.4%	48.0%	50.0%	50.5%	49.3%	52.0%
	O 1s	530.8	29.6%	31.2%	31.5%	31.0%	32.0%	31.0%	31.2%
		532.5	15.0%	10.4%	9.5%	9.5%	9.3%	9.5%	9.0%
	F 1s	685.2	0%	0.7%	0.5%	0.3%	0.5%	0.6%	0.3%
		688.7	0%	0%	0%	0%	0%	0%	0%
Deposited at 100 °C	C 1s	285.0	19.0%	8.5%	10.0%	8.5%	9.0%	8.0%	7.0%
	Zn 1s	1022.5	34.0%	47.0%	48.0%	49.0%	49.0%	49.5%	50.0%
	O 1s	530.8	25.5%	32.5%	30.0%	30.5%	30.0%	30.5%	31.0%
		532.5	18.0%	10.0%	10.5%	10.0%	10.0%	10.0%	10.0%
	F 1s	685.2	0%	2.0%	1.5%	2.0%	2.0%	2.0%	2.0%
		688.7	0%	0%	0%	0%	0%	0%	0%
Deposited at 150 °C	C 1s	285.0	9.6%	6.7%	5.7%	5.0%	3.8%	3.1%	3.6%
	Zn 1s	1022.5	32.4%	39.0%	43.5%	45.2%	44.2%	45.3%	45.4%
	O 1s	530.8	25.2%	29.6%	30.5%	33.0%	33.0%	33.2%	33.5%
		532.5	16.2%	13.0%	11.5%	10.7%	10.2%	10.4%	10.2%
	F 1s	685.2	0%	1.7%	0.8%	1.1%	1.1%	1.6%	0.8%
		688.7	0%	0%	0%	0%	0%	0%	0%

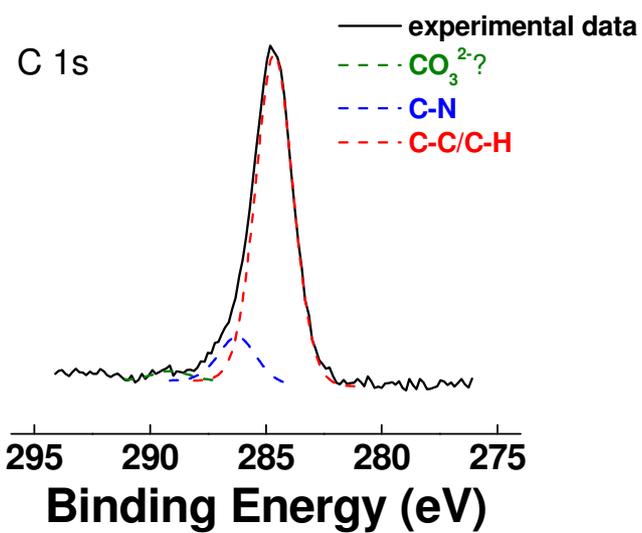


Figure S3. Deconvolution of the C1s XPS spectra feature from films electrodeposited at 150 °C.

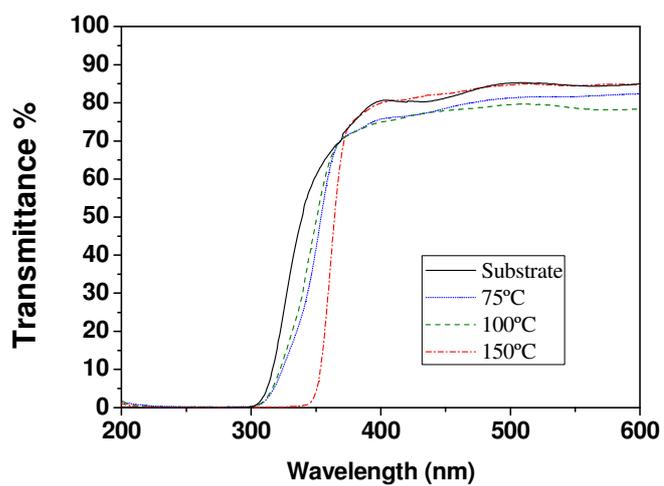


Figure S4. Optical transmittance spectra of the naked substrate and three samples electrodeposited at different temperature.