Role of direct and inverted undoped Spiro-OMeTAD - perovskite architectures in determining solar cells performances: an investigation via electrical impedance spectroscopy

Marianna Ambrico, Paolo F. Ambrico, Luisa De Marco, Rosabianca Iacobellis, Arianna D'Abramo, Teresa Ligonzo*

Supplementary Material.

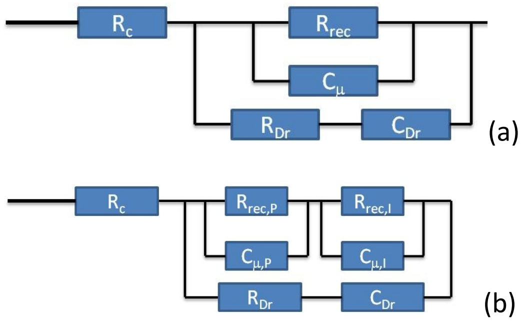

Figure S.1 (a) Circuit 1 used for the best fitting of NPs of single layers and inverse Spiro-OMeTAD/ Perovskite (P-I) interface; (b) circuit adopted for best fitting of NPs in direct Perovskite/ Spiro-OMeTAD interface (I-P)

Table S.1 Best fit parameters of Spiro-OMeTAD and Perovskite single layer NPs (see text);

V_{DC} [V]	C_{Dr} [nF]	Err [%]	C_μ [pF]	Err [%]	R_{rec} [Ω]	Err [%]	R_{Dr} [Ω]	Err [%]
Perovskite (Circuit (a))	8.2	2.0	81	8.3	2671	1.2	119	2.0
Spiro-OMeTAD (Circuit (a))	2.4	4.0	224	20	648	1.8	35	5.4

V_{DC} V	C_{Dr} nF	Err %	$C_{\mu,P}$ nF	Err %	$C_{\mu,I}$ nF	Err %	$R_{rec,P}$ Ω	Err %	$R_{Rec,I}$ [Ω]	Err %	R_{Dr} [Ω]	Err %	ζ (a.u)	τ_1 (μs)	τ_2 (μs)
Direct															
0.0 V	1.9	5.7	6.1	3.4	6.3	2.6	6872	6.4	39952	1.5	4612	11	1.20	92	52
0.6	0.2	4.0	=	=	3.0	1.1	56	4.0	29291	1.5	97589	1.7	0.09	20	2.6
-0.6(direct pol.)	1.7	11	7.6	5.7	5.9	1.5	201	8.0	18819	1.7	13027	19	0.30	25	21
Inverted (Circuit (a))															
0.0	0.1	2.0	-	-	7.7	2.0			10851	1.0	81	5.0	0.7	85	0.6
0.6 (direct pol)	5.0	2.0			11.0	2.0			4294	1.2	112000	3.0	0.2	630	132
-0.6	7.6	3.0			7.16	2.0			7488	1.3	85	2.0	0.1	111	0.7

P=Spiro-OMeTAD, I=Perovskite

Table S.2 Best Fit parameters of direct (I-P) and inverted (P-I) Spiro-OMeTAD-Perovskite interfaces and corresponding polarization and recombination times as recalculated by adapting the Bisquert model (ref. in text) to our modeling.

Reformulation of τ_1 and τ_2

Considering the electrical circuit (a) and (b) and that the extracted parameters do not satisfy the condition $C_{dr} >> C_{\mu}$ we recalculated the impedance (here expressed via the admittance $Y= Z^{-1}$) as:

In circuit (a)

$$Y = \frac{1}{Z} = \frac{1}{R_{rec}} + i\omega C_{\mu} + \frac{1}{R_{dr} + (1\omega C_{dr})^{-1}} \tag{1}$$

and in circuit (b) as

$$Y = \frac{1}{Z} = \frac{1}{R_{rec,I}} + i\omega C_{\mu,I} + \frac{1}{R_{rec,P}} + i\omega C_{\mu,P} + \frac{1}{R_{dr} + (i\omega C_{dr})^{-1}}$$

(2)

Then in circuit (a) the equation develops in the same fashion seen in ref.1:

$$Z = \frac{1}{Y} = R_{rec}\left[1 + i\omega C_{\mu} R_{rec} + \frac{i\omega C_{dr} R_{rec}}{1 + i\omega C_{dr} R_{dr}}\right]^{-1}$$

(3)

But since $C_{\mu} \propto C_{dr}$ the expression of the impedance Z is :

$$Z = R_{rec}\left[\frac{1 + i\omega C_{dr} R_{dr} + i\omega C_{\mu} R_{rec} + (i\omega)^2 R_{dr} C_{\mu} C_{dr} R_{rec} + i\omega C_{dr} R_{rec}}{1 + i\omega C_{dr} R_{dr}}\right]^{-1}$$

(4)

That can be reformulated as:

$$Z = R_{rec}\left[\frac{1 + i\omega C_{dr}\left(R_{dr} + R_{rec}\left(1 + \frac{C_{\mu}}{C_{dr}}\right)\right) + (i\omega)^2 R_{dr} C_{dr} C_{\mu} R_{rec}}{1 + i\omega C_{dr} R_{dr}}\right]^{-1}$$

(5)

and reduces to expr.36 of ref. 19 (main text) if $C_{dr} >> C_{\mu}$.

In circuit (b) the final expression was similar to expr.(5) but by R_{rec} replaced by:

$$R_{rec,eq} = \frac{R_{rec,I}\, R_{rec,P}}{R_{rec,I} + R_{rec,P}}$$

(6)

And $i\omega C_{\mu}$ by

$$i\omega C_{\mu,eq} = i\omega\left(C_{\mu,I} + C_{\mu,P}\right)$$

(7)

Finally by following the similar procedure of ref.19 (main text) we placed

$\tau = \sqrt{R_{dr} C_{dr} C_{\mu} R_{rec}}$ *in circuit* (a) *or* $\tau = \sqrt{R_{dr} C_{dr} C_{\mu,eq} R_{rec,eq}}$ *in circuit* (b)

And in circuit (a)

$$\gamma = \frac{\sqrt{R_{dr}C_{dr}C_{\mu}R_{rec}}}{C_{dr}\left(R_{dr} + R_{rec}\left(1 + \frac{C_{\mu}}{C_{dr}}\right)\right)}$$

Digitare l'equazione qui.

And in circuit (b)

$$\gamma = \frac{\sqrt{R_{dr}C_{dr}C_{\mu,eq}R_{rec,eq}}}{C_{dr}\left(R_{dr} + R_{rec,eq}\left(1 + \frac{C_{\mu,eq}}{C_{dr}}\right)\right)}$$

The estimate of γ via the extracted best fit parameters returned a value lower than 1 except in the case of the direct structure with no bias applied where it was found slightly higher than 1. (see Table S.2)

Therefore, since we were interested to the behaviour of the interface under bias, we approximate for all biases the calculation by using the same kind of factorization procedure in ref.19, although taking into account the correction due to $C_{\mu} \propto C_{dr}$;

$$Z = \frac{1 + \frac{i\omega\tau}{\gamma}}{(1 + i\omega\tau_1)(1 + i\omega\tau_2)} R_{rec}$$

With τ_1 the dielectric polarization time and τ_2 the recombination time.

In circuit (a):

$$\tau_1 = C_{dr}\left(R_{dr} + R_{rec}\left(1 + \frac{C_{\mu}}{C_{dr}}\right)\right)$$

and

$$\tau_2 = \frac{R_{rec}\,R_{dr}}{\left(R_{dr} + R_{rec}\left(1 + \frac{C_{\mu}}{C_{dr}}\right)\right)} C_{\mu}$$

In circuit (b) the expressions were basically the same but with R_{rec} and C_{μ} replaced by $R_{rec,eq}$ and $C_{\mu,eq}$.

[S1] J. Bisquert, L. Bertoluzzi, I. Mora-Sero and G. Garcia-Belmonte, Theory of Impedance and Capacitance Spectroscopy of Solar Cells with Dielectric Relaxation, Drift-Diffusion Transport, and Recombination, *J. Phys. Chem. C*, 2014, **118**, 18983–18991.