

COMMENT

[View Article Online](#)
[View Journal](#) | [View Issue](#)Cite this: *J. Mater. Chem. A*, 2022, 10, 8594Received 25th January 2022
Accepted 14th March 2022

DOI: 10.1039/d2ta00706a

rsc.li/materials-aReply to the 'Comment on "Flat band potential determination: avoiding the pitfalls"' by M. I. Díez-García, D. Monllor-Satoca and R. Gómez, *J. Mater. Chem. A*, 2022, 10, DOI: 10.1039/D1TA06474FAnna Hankin *^a and Franky E. Bedoya-Lora ^b

The comment of Díez-García and co-workers on the article 'Flat band potential determination: avoiding the pitfalls' is a very valuable contribution to the discussion about the appropriateness of various models and techniques used for the determination of flat band potentials of semiconducting photoelectrodes, as well as other parameters. Such discussions will benefit the community and should improve the reliability of published parameters characterising photoelectrode interfaces with electrolytes. Herein we respond to the specific topics addressed in the comment: (i) the correction of the geometric photoelectrode surface area by surface roughness to enable more accurate characterisation of materials with nanotextured surfaces and (ii) the inclusion of photon flux limitation in the Gärtner–Butler model.

Mott–Schottky analysis – geometric surface area vs. real surface area

We agree that if a roughness factor (r) of a semiconductor surface is known, then the geometric surface area (A_{geom}) can be replaced with a real surface area (A_{real}) in the Mott–Schottky equation, as shown in eqn (1) in ref. 1 and also in eqn (1) below, by substituting $A_{\text{real}} = r \times A_{\text{geom}}$.

$$\frac{A_{\text{geom}}^2}{C_{\text{SC}}^2} = \frac{2}{e\epsilon_r\epsilon_0 N_D r^2} \left(U - U_{\text{FB}} - \frac{kT}{e} \right) \quad (1)$$

In this updated formulation, C_{SC} denotes the space charge layer capacitance in the unit of farads (not normalised by the surface area), ϵ_0 represents the permittivity of free space, ϵ_r is the relative permittivity (dielectric constant) of the semiconductor, e is the electronic charge, N_D is the density of donor states (carrier density), and U and U_{FB} denote the applied potential and the flat band potential, respectively. In doing so, the apparent violation of one of the assumptions underpinning the Mott–Schottky equation – “The semiconductor surface is perfectly smooth” – is nullified, as pointed out by the authors of ref. 1. We agree with this, except for the situation where the dimensions of the nano-features, such as nanowires or dendrites, are comparable with the width of the semiconductor space charge layer.² If this is the case, the depletion layer thickness could be highly non-uniform across the surface of the semiconductor, leading to effective surface area

values, $A_{\text{geom}} \leq A_{\text{effective}} \leq A_{\text{real}}$, that will change as a function of applied potential and would be expected to results in non-linearity of the Mott–Schottky plot. These effects have been reported and discussed in more detail by Cesar *et al.*³ and Mora-Seró *et al.*⁴

Gärtner–Butler model – requirement of photocurrent limitation by the incident photon flux

We agree that the original Gärtner–Butler equation, which we used to model the photocurrent as a function of band bending in ref. 2, did not include a limitation by the photon flux. Although we imposed such a constraint in several of our other publications,^{5–7} where we modelled the photocurrent, we did not do so in ref. 2. Hence, we agree with the authors of ref. 1 that our predicted photocurrents were not constrained by the maximum value that could be generated at 100 mW cm^{−2} irradiance.

Imposing a limitation on the photocurrent, j_{photo} , by photon flux ($I_0 e$) in the denominator of eqn (2), would limit the effect of high doping levels on the proportion of applied potential that is dropped across the Helmholtz layer rather than across the depletion layer.

$$j_{\text{photo}} = \frac{\alpha_i I_0 \left(\frac{2e\epsilon_0\epsilon_r}{N_D} \right)^{\frac{1}{2}} (\Delta\phi_{\text{sc}})^{\frac{1}{2}}}{\left(1 + \frac{\alpha_i I_0 \left(\frac{2e\epsilon_0\epsilon_r}{N_D} \right)^{\frac{1}{2}} (\Delta\phi_{\text{sc}})^{\frac{1}{2}}}{I_0 e} \right)} \quad (2)$$

^aDepartment of Chemical Engineering, Imperial College London, London, SW7 2AZ, UK. E-mail: anna.hankin@imperial.ac.uk

^bLaboratory of Renewable Energy Science and Engineering, Institute of Mechanical Engineering, École Polytechnique Fédérale de Lausanne, 1015, Lausanne, Switzerland

Comment

Symbols in eqn (2) represent: j_{photo} – photocurrent density, $\Delta\phi_{\text{sc}}$ – band bending at the semiconductor interface, λ – wavelength, α – absorption coefficient, I_0 – incident photon flux; the remaining parameters were defined in the above text.

Further, as explained in ref. 3, other important corrections can be made to eqn (2) to account for (i) bulk recombination, (ii) surface recombination and (iii) a spectrally resolved absorption coefficient.⁵

Author contributions

The authors prepared this response jointly and with equal contributions.

Conflicts of interest

There are no conflicts to declare.

References

- 1 M. I. Díez-García, D. Monllor-Satoca and R. Gómez, *J. Mater. Chem. A*, 2022, **10**, DOI: 10.1039/D1TA06474F.
- 2 A. Hankin, F. E. Bedoya-Lora, J. C. Alexander, A. Regoutz and G. H. Kelsall, *J. Mater. Chem. A*, 2019, **7**, 26162–26176.
- 3 I. Cesar, K. Sivula, A. Kay, R. Zboril and M. Gratzel, *J. Phys. Chem. C*, 2009, **113**, 772–782.
- 4 I. Mora-Seró, F. Fabregat-Santiago, B. Denier, J. Bisquert, R. Tena-Zaera, J. Elias and C. Lévy-Clément, *Appl. Phys. Lett.*, 2006, **89**, 203117.
- 5 A. Hankin, F. E. Bedoya-Lora, C. K. Ong, J. C. Alexander, F. Petter and G. H. Kelsall, *Energy Environ. Sci.*, 2017, **10**, 346–360.
- 6 F. E. Bedoya-Lora, A. Hankin and G. H. Kelsall, *J. Mater. Chem. A*, 2017, **5**, 22683–22696.
- 7 F. E. Bedoya-Lora, A. Hankin and G. H. Kelsall, *Front. Chem. Eng.*, 2021, **3**, 749058.

