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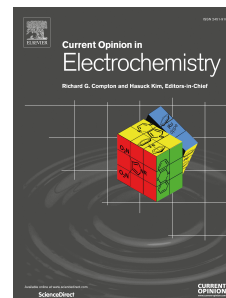
Nanoporous Carbons for the Electrochemical Reduction of CO$_2$: challenges to discriminate the roles of nanopore confinement and functionalization

Alicia Gomis-Berenguer[1], Elhassan Amaterz[2], Sebastian Torres[1], Jesús Iniesta[1*], Conchi Ania[2*]

[1]Institute of Electrochemistry, University of Alicante, 03080 Alicante, Spain

[2]CEMHTI, UPR 3079 CNRS, Univ. Orléans, 45100 Orleans, France

*Corresponding authors: jesus.iniesta@ua.es; conchi.ania@cnrs-orleans.fr

Abstract

The use of porous carbons in the electrochemical reduction of CO$_2$ (CO2ER) has become an active research area. Despite good faradaic efficiencies and production rates, understanding their electrocatalytic activity is challenging owing to the complexity of the CO$_2$-nanoporous carbon interactions. In this opinion review, we emphasize on the critical importance of discriminating the impacts of nanopore confinement and surface functionalization of porous carbons on the CO2ER. We have performed a rational analysis of recent literature addressing this topic, comparing electrocatalytic performance with knowledge about CO$_2$-porous carbon affinity. Reported data has been re-discussed focusing on a complete characterization of the carbon electrodes to correlate physicochemical characteristics and the electrocatalytic activity. A perspective view is provided for future directions on the use of porous carbons in the CO2ER.

Keywords: nanoporous carbons, nanoconfinement, metal-free electrocatalysts, surface functionalization

Introduction

In a world that urgently needs to redress the balance of energy derived from fossil fuels, an efficient and selective conversion of CO_2 into fuels and chemicals appears as a promising solution. Among different technological approaches, the electrochemical reduction of CO_2 (CO2ER) is an attractive alternative due to its mild operating conditions (ambient temperature, atmospheric pressure, neutral pH). Main challenges are related to the search for sustainable electrocatalysts with high activity and controlled selectivity towards C2 products over C1 compounds, due to the higher energy storage power of the former [1,2].

Known electrocatalysts for this reaction are mainly noble metals (e.g., Au, Ir, Pd) [1,3] and metal alloys and their oxides (e.g., Cu, Sn, Cu_xO_y, Sn_xO_y, Co_xO_y) [4-6]. Triggered by the multiple disadvantages of metal-based catalysts (cost, scarcity, durability) a vast number of other materials are being explored; particularly, the research on metal-free abundant catalysts has become a priority [7-9].

In this context, carbon materials are frequently used in electrochemical reactions as supports of electrocatalysts, to ensure large electrochemically active surfaces and/or to improve the dispersion and loading of metals (e.g., glassy carbon, carbon paper, carbon cloth) [8,10]. Furthermore, their potentialities as metal-free electrocatalysts themselves have been demonstrated in various electrochemical reactions for many different forms of carbon (graphene, carbon nanotubes, carbon nitride, nanoporous carbons), with some examples showing outcompeting performance and durability than state-of-the-art metallic electrocatalysts [9].

Nanoporous carbons have inherent advantages for electrochemical reactions: tailorable porosity and surface chemistry, abundance of active sites, ability to support large pH gradients, high surface area, high stability and resistance to corrosion in various environments, abundance and sustainability, good electric conductivity (compared to graphite or graphene). Moreover, they display a good wettability (i.e., electrolyte diffusion inside the nanopores) [11] and high CO_2 adsorption capacities [12]. The latter is an essential prerequisite step for the electrochemical reduction of CO_2, although often overlooked. Although not much explored for the CO2ER, most efforts have focused in introducing modifications to tailor the electrocatalytic centers of the carbon materials via doping [13-18] or nanopore control [19-22]. The improved performance (described in terms of conversion, faradaic efficiency, selectivity) has been mainly attributed to the effect of heteroatom doping on the electronic properties of the carbon material, and/or creating specific electrocatalytic active sites [23,24]. Two main challenges of most carbon-based electrocatalysts are their still rather low production rates and that selectivity seems to be mostly dominated by the formation of CO and CH_4, as opposed to metal-based electrocatalysts where methanol, formic acid and other C2 compounds have been reported.

The role of the nanoporosity has also attracted the attention, with more emphasis on carbons displaying mesopores (2-50 nm) and macropores (> 50 nm) [20, 22, 25, 26], while the benefits of

a microporous network (< 2 nm) is less investigated and often neglected [26-29]. The area is in its infancy owing to the complexity of nanoporous carbon electrocatalysts, and yet much work needs to be done in the appropriate direction. In this opinion review, the authors address the challenges associated to discriminating the roles of nanoporosity and surface chemistry to understand the electrocatalytic activity of nanoporous carbons in the CO2ER. This opinion review emphasizes on the need to carry out a rational design and characterization of the nanoporous carbon electrocatalysts to take into consideration both aspects, so as to understand the real impact on the Faradaic efficiency (FE) of products from CO_2 conversion and on the selectivity of the reaction.

Nanoconfinement and surface functionalization

The concept of spatial confinement in pores of nanometric dimensions combined with appropriate catalytic active sites as relevant parameters for controlling conversion yields, FE values and or selectivity of electrochemical reactions has been recently addressed in the literature [30-34], although it is not yet fully understood (and it is often overlooked). Advantages of nanoscale confinement to electrocatalytic performance are related to improved selectivity, conversion and kinetics of electrochemical reactions, as well as the stability and recyclability of the catalysts. Since electrochemical reactions occur at the catalyst/electrolyte interface, such enhancements are attributed to the modification of the properties in the nanoconfined space. As an example, nanopore confinement has an impact on the reactant's or intermediates concentrations, thus affecting the overall reaction kinetics compared to bulk reactions. This is typically controlled by the size, shape and connectivity of the nanopore architecture, rather than to the surface area [30,34]. Nanoconfinement is also known to favor the collision frequency of the reactants with the electrode surface (due to short diffusion lengths). As a result of the extremely confined spatial environment and the interactions with the pore walls, trapped reactant molecules remain longer near the surface, leading to large current amplifications, shifts to positive onset potentials and enhanced electrocatalytic conversions and selectivities [32]. Modulating the surface chemistry (composition) of the catalysts is also a well-known strategy to create energetically favorable active sites with varied affinity towards the reactant molecules (thus governing the strength of interfacial interactions).

In this regard, three-dimensional nanoporous carbon electrocatalysts can be described as nanoreactors where the electrocatalytic performance can be modulated by the complex interplay of those aspects at the interfacial region, governed by the size, composition and connectivity of the nanopores. Thus, an efficient carbon electrocatalyst for CO2ER is expected to display two main characteristics (Scheme 1A): (1) an adequate nanopore architecture of interconnected channels of adequate dimensions to boost electrode-CO_2 interactions via nanoconfinement effects, and (2) a balanced composition with surface functional groups capable of activating CO_2

molecules. All of it without sacrificing other important parameters of the carbon electrode as wettability or electrical conductivity [11,35,36].
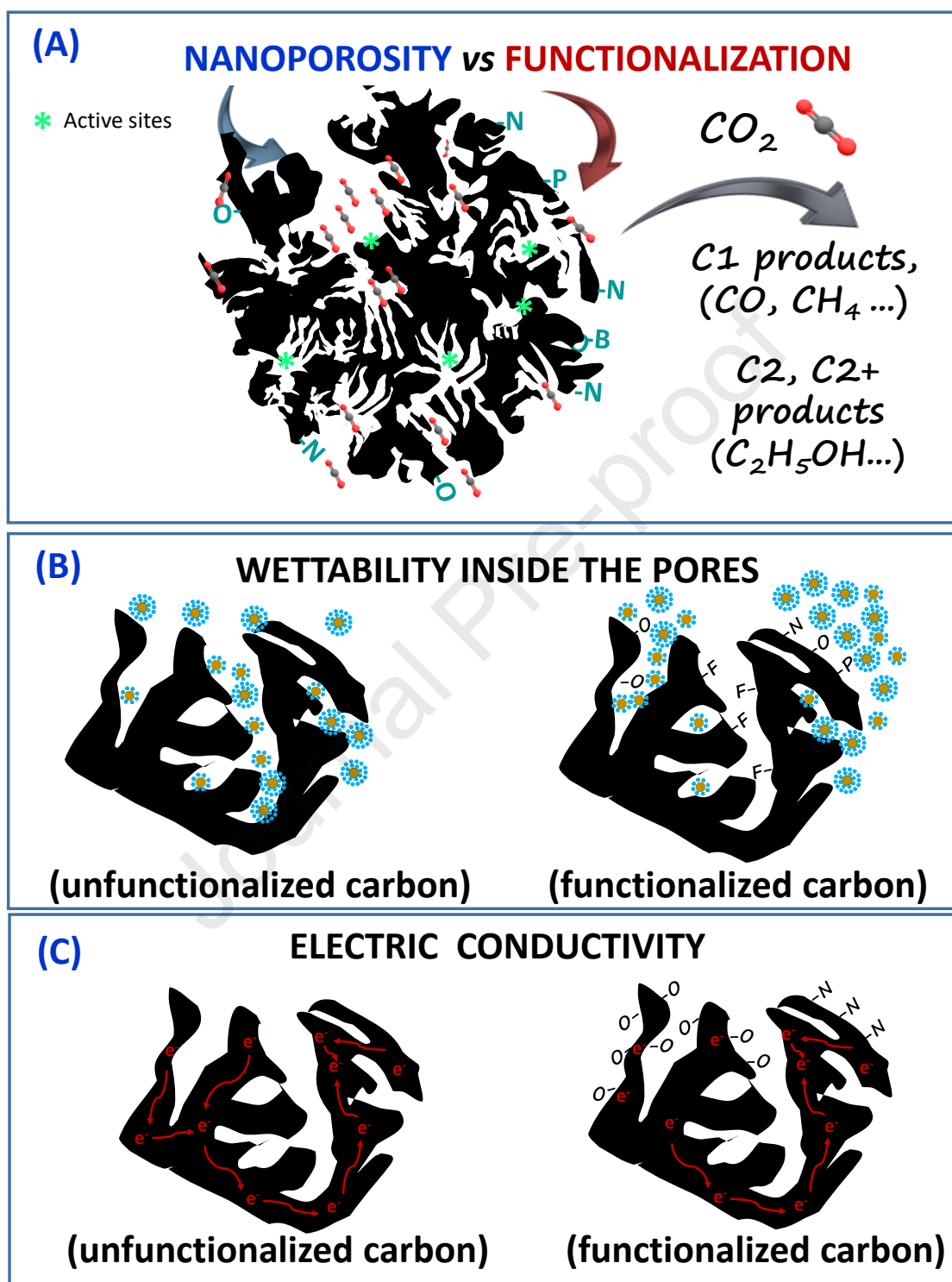
Scheme 1. Complexity of nanoporous carbon electrocatalysts depending on the balance between porosity (size and accessibility), composition (heteroatom doping), wettability and electrical conductivity, defining the electrocatalytic active sites (*) and the outcome of CO2ER. (A) porosity and surface chemistry are simultaneously illustrated depicting the selectivity of the catalysts towards C1, C2 products and beyond; impact of surface functionalization on the (B) wettability and (C) electric conductivity of the carbon materials.
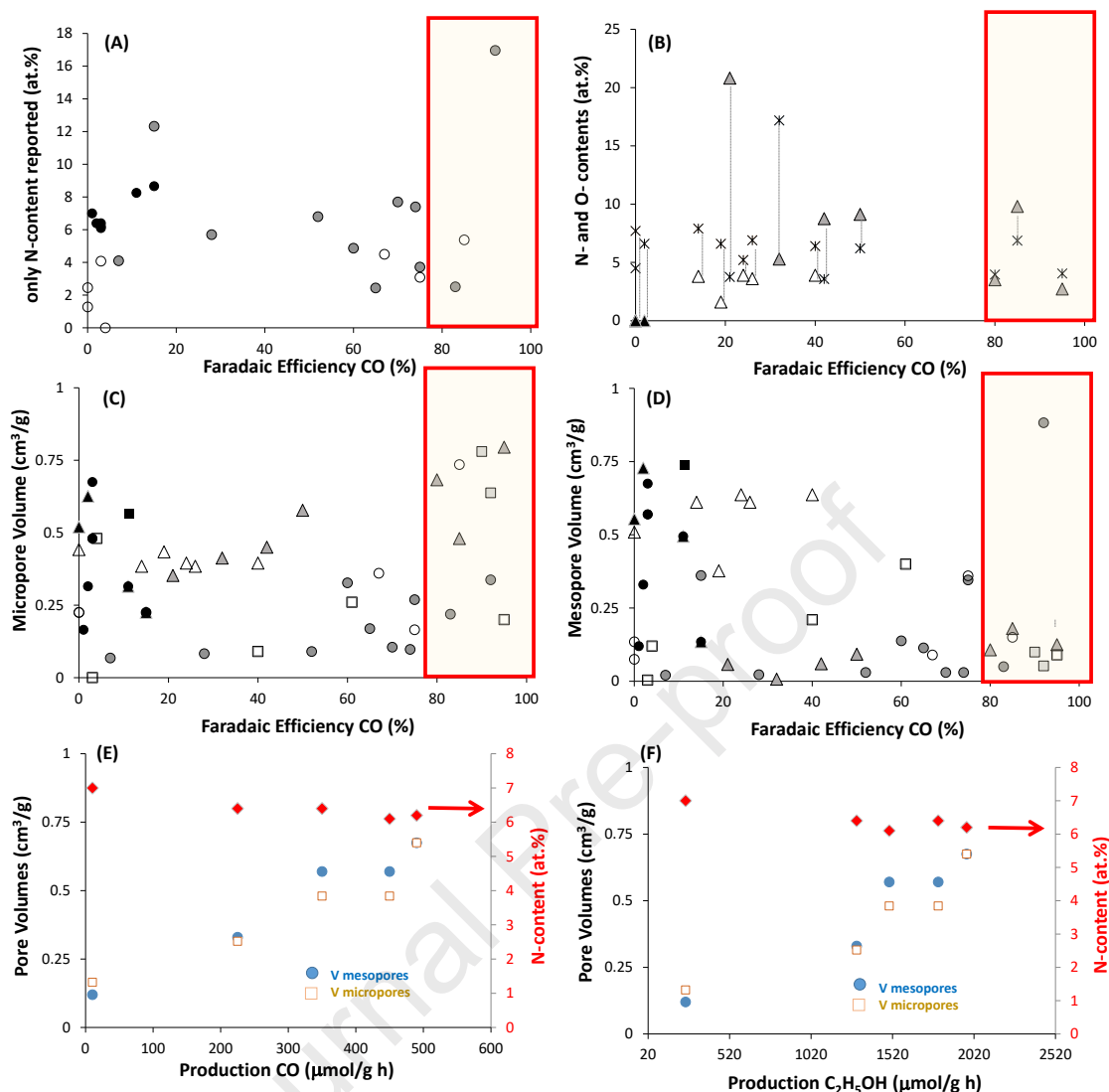
Figure 2. (A-D) Correlation between faradaic efficiency of CO and the (A) nitrogen content -data of other heteroatom is not provided-; (B) nitrogen and oxygen content; (C) micropore volume; (D) mesopore volume. Data reported in references [14,15,17-19,22,25-29,40] has been herein re-analyzed and plotted to build the correlations. Symbols in plots (A-D) represent different composition: circles (only N-data is reported); triangles (N- and O- are reported); squares (N- or O-content below 3 at.%, arbitrarily chosen as low functionalization). Colors of the symbols in plots A-D represent different applied potentials (vs RHE): black symbols (-0.60 V), grey symbols (-0.67 V), white symbols (-0.90 V). Stars in plot D indicate the O-content of the corresponding N-doped carbon (lines are a guide for the eye). Red rectangles in plots A-D highlight FE over 80%. (E,F) Correlation between production rates of carbon monoxide (E) and ethanol (F) and selected textural parameters (micropore and mesopore volume) and N-content of a series of carbon electrocatalysts.

Regarding the composition, there seems to be general agreement about the beneficial effect of heteroatom doping to achieve high CO_2 conversions and FE, associated to the electronic properties' modulation of the doped carbon [21,37]. Knowledge from the adsorption field on the use of nanoporous carbons for the storage/separation of CO_2 has shown that the existence of specific interactions of CO_2 (through its quadrupole moment) with surface groups (e.g., acid-base,

polar and hydrogen bonding) explains the affinity of CO_2 towards the surface of functionalized carbons [38], triggering a higher degree of nanopore space utilization.

Hence, heteroatoms doping is an interesting strategy for the CO2ER. Even though most studies deal with N-doping [13-17, 25-28], recent studies have shown the benefits of doping and dual co-doping with other elements (e.g., O- [19], B- [24], S- [21], P- [39]). Further research should be drawn in this direction. On the other hand, the functionalization of carbon materials is quite challenging, and very often the obtained carbon shows a variety of moieties and various heteroatoms.

As an example, N-doped carbons typically display high amounts of oxygen groups, despite of which the latter is often not quantified nor considered in the discussion. This has been illustrated in Figures 2A, 2B, where the authors show correlations redrawn from data available in the literature between the electrocatalytic activity and the nitrogen and/or oxygen content of carbon materials. We have chosen the faradaic efficiency towards CO production as the indicator of the electrocatalytic activity due to the abundance of data in the literature (and scarce records on carbon electrocatalysts rendering other products). As seen, there is not a direct correlation between the N- and/or O-contents and the faradaic efficiency, since the higher FE were obtained with those carbons with moderate heteroatom content. This is a due to the complexity of the analysis given the disparity of textural properties of those functionalized carbons (Figures 2C, 2D). Hence, reporting disaggregated data on porosity and composition, and the complete characterization of the nature of surface groups (beyond heteroatom content) would be advisable (e.g., useful characterization techniques may be XPS, TPD-MS, IR...).

In addition, the modification of the surface chemistry of carbon materials is known to affect the wettability and electric conductivity [36] (this is illustrated in Scheme 1B, 1C). As an example, the conductivity of a given carbon matrix (low or non-functionalized) drops upon O-functionalization unlike the incorporation of N-moieties (Scheme 1C). These aspects are scarcely considered, and should be discussed to fully analyze the role of the surface moieties as electrochemical active sites.

Role of nanoporosity

The porosity is also a key parameter that controls the CO_2-carbon electrode interactions, which is expected to have a large impact on the electrocatalytic activity. Again, important lessons learned from the field of adsorption should be borne in mind. Micropores (< 2 nm) and narrow micropores (< 0.7 nm) are known to govern the adsorption of CO_2 at atmospheric pressure in nanoporous carbons, whereas wider micropores and small mesopores define the uptake at high pressures [41-44]. Analogously, high surface areas and micropore volumes seem to favor the electrocatalytic conversion of CO_2 [26,27,29,40], although the dependence with different performance indicators is not clear due to the diversity of compositions (Figures 2C, 2D). Indeed, high FE can be obtained

irrespectively of the use of with microporous and mesoporous carbons, although FE values over 80% are predominantly obtained in the presence of microporosity, pointing to the role of nanoconfinement.

As a general rule, the increase catalytic activity with the porosity is attributed to an increased exposure to active sites; deeper analyses of the micropore structure have revealed that carbon materials with micropores centered at ca. 0.5 and 1.3 nm exhibit high FE and low free-energy barrier, due to a fast diffusion of CO_2 [40]. In addition, it has also been reported that carbons showing ultra-micropores (between 0.7-2 nm) exhibit selectivity towards CH_4 [19] and ethanol [29]. The later study has appealed to the desolvation of the reactants in the micropores that would facilitate coupling reactions to form C1 intermediates.

It should be pointed out that as the average pore size of the electrode material matches that of CO_2, the CO_2-porous catalyst interactions become stronger (assuming an adequate chemical affinity) and are expected to favor the charge transfer at the nanopore level. This is evidenced in the isosteric heat of adsorption values reported for nanoporous carbons (indicative of thermodynamically favorable sites), ranging from ca. 20-25 kJ/mol for un-doped carbons [41, 44] with different pore networks, and ca. 35-55 kJ/mol for doped carbons [45,46]. It also highlights the importance of separating the impact of pore size from that of surface chemistry when analyzing carbon-CO_2 interactions.

Despite these promising results, few studies deal with exploring microporous carbons for CO2ER. This might be due to the typically small current densities obtained (as a result of the typically poor conductivity in microporous carbons). However, recent advances in the synthesis of carbon materials have enabled to prepare carbons with high surface areas and controlled micropores [47]. Such systems may offer interesting opportunities for the selectivity of the electrochemical conversion of CO_2 in micropore confined spaces [48].

As opposed to microporosity, the role of mesoporous/macroporous carbons has been more investigated for CO2ER [25]. In a recent study, Hursan et al reported the electrocatalytic activity of a series of N-doped carbons with similar composition and controlled meso-/macro-porosity (pores of sizes ca. 13, 27 and 90 nm) [26]. Although the electrocatalytic activity was misleading interpreted in terms of the "morphology" of the electrodes, rather than the pore size (the carbons displayed similar pore shapes), the study demonstrates the benefits of narrow mesopores over macropores. Furthermore, an interesting correlation is shown between the electrocatalytic activity and the CO_2 adsorption strength on the carbon materials, evaluated upon characterization by temperature programmed desorption (a common technique in materials chemistry, not so popular in the field of electrochemistry).

Besides the impact in conversion, the size of mesopores seems to be important to boost the selectivity of CO over H_2 (confinement effects) [26], while the geometry of nanopores would favor the selectivities for C2 compounds, pointing out the easier dimerization of intermediates in

cylindrical carbon nanopores [22]. Furthermore, the integration of nanoporous carbons in other 3D hierarchical structures with interconnected channels has also been beneficial for improving the three-phase contact in CO2ER, and a faster transport of reactants/products from/to the electrolyte [24,49]. In such materials, the macropores assure an efficient mass transport, while mesopore/micropore network provides the electroactive sites. The challenge still remains in the preparation of these structures at large scale (and their stability) [15]. Owing to the aforementioned complex scenarios, the impact of nanoconfinement should be as much as possible decoupled from the surface functionalization on carbon materials in order to extract solid conclusions from the nanoconfinement effects. Unfortunately, very few studies in the literature consider this approach, and very often incomplete datasets (composition and porosity) are reported, with discussion lacking from adequate correlations between the electrocatalytic performance and the relevant physicochemical parameters of the carbon electrode. This has been illustrated in Figures 2E, 2F for carbons with similar functionalization extents. As seen, a correlation can be observed between the production rates of CO and ethanol and the volumes of micropores and mesopores. It is also noticeable that FE between 60-80% are mainly obtained at moderate electrode potentials.

Another challenge is to synthesize adequate control materials to isolate the effects of porosity from those of surface chemistry. Very often the synthetic approach followed to obtain carbons with controlled pore architectures and high functionalization (e.g., soft/hard templating, sol-gel methods with adequate choice of precursor, post-synthetic functionalization) [47] cannot be used to prepare un-doped materials with similar porosity, or non-porous doped materials with identical composition. Hence, a complete physicochemical and morphological characterization of the electrocatalysts is compelling to analyze the electrocatalytic activity and discuss it considering the contributions of the different factors (Figure 3).
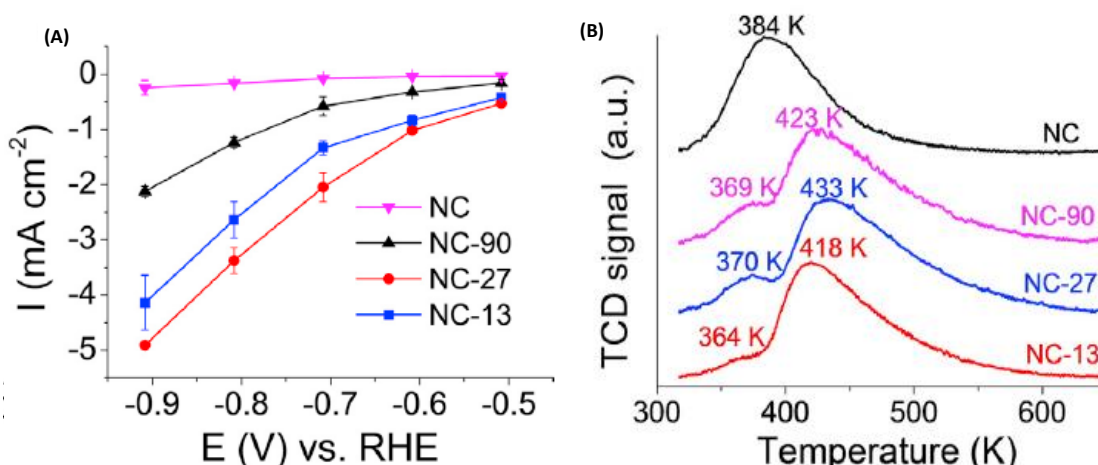
Figure 3. Electrochemical reduction performance on mesoporous carbons with controlled mesopore size showing (A) the normalized total current densities after 40 min of electrolysis in 0.1M $KHCO_3$ solution saturated with CO_2; (B) the temperature programmed CO_2 desorption

profiles of the studied catalysts to reveal the role of CO_2-carbon affinity in the selectivity. Reprinted with permission from [26].

Metrics of merit in electrochemical performance of CO2ER

The faradaic efficiency and selectivity are the most relevant parameters used in the literature to analyze the CO2ER. The reduction products -both gases and liquids- are diverse and complex and various analytical tools should be employed to confirm them (e.g., GC, HPLC, MS, NMR). To evaluate the technological and economic viability of a potential scaling-up, more attention should be paid to the long-term stability of the electrodes and to other electrochemical parameters such as production rates of products, analysis of the current densities, overpotentials, or charge passed. These are poorly (even unmentioned) discussed in the literature. One of the scarce exceptions is shown in Figures 2E, 2F, where the production rates of CO and ethanol are reported for a series of carbons with similar N-content, and can be correlated to the pore volumes (micropores and mesopores). Another metric of merit that should be considered is the concentration of products obtained, since further separation/recovery may be difficult. In this regard, the choice of electrolyser (e.g., filter-press, half/full polymer electrolyte membrane cell configurations) is crucial and will dictate subsequent physicochemical stages.

In general, commonly reported description includes: electrode potentials, mostly evaluated from chronoamperometric techniques without any iR drop correction; electrical conductivities of the carbon materials and/or electrodes are rarely reported; a rational comparison of electrolysis should be carried out at similar passed charge; current densities should be normalized to the estimated electrochemical active surface area of the catalyst by providing the capacitance per projected area or mass, F/m^2 or F/g (rather than geometric or specific surface area) to account for roughness of the electrodes. This is also connected to the catalyst ink formulation and the preparation of the electrodes (i.e., ink deposition, catalyst layer formation) having consequences on the rheology and electrochemical properties [50]. The latter issues are becoming critical for electrodes of small dimensions (ca. few mm^2).

Similarly, Tafel slopes are often reported to evaluate the electrocatalytic performances, but this parameter should be handled with care when used for screening nanoporous materials. Tafel slope values rely on current voltage data at kinetic control regime, and often porous catalysts may encounter CO_2 diffusion limitations (e.g., transport limitations in the electrolyte, poor CO_2 concentration in the electrolyte, irregular CO_2 concentration inside the porosity) that can affect the discrimination of the kinetic from the limiting current regimes. As a result, significant errors may be induced in the estimation of the Tafel values [51].

Conclusions and outlook

The use of nanoporous carbons as electrocatalysts for CO2ER is expected to attract further attention in the forthcoming years, due to the need to obtain sustainable catalysts for replacing (noble) metals. While substantial progress has been made in the synthesis of carbon materials with controlled nanopore architectures and tailor-designed active sites, it is clear that further attempts are needed to rationalize the interplay between their electrocatalytic performance with the porosity (size/connectivity of nanopores) and composition (nature of groups).

To unravel the practical feasibility of nanoporous carbons for CO2ER, two major directions should be considered. The first one is related to improving the understanding of the factors governing the CO_2-carbon interaction and the electrocatalytic activity of carbon cathodes. This can only be achieved by coupling the knowledge on electrochemistry with that from other disciplines (e.g., adsorption) and by performing a complete characterization of the carbon electrodes. As an example, the preferential CO_2 adsorption sites on carbon surfaces should be analyzed as potential electroactive sites for the target reaction. Recent computational CO2RR studies have pointed out directions for elucidating electroactive sites and reactions mechanisms; this could be the grounds for flourishing cooperation between disciplines.

Another foremost priority is discriminating the roles of porosity and surface chemistry, since both parameters seem to be relevant strategies to promote selectivity beyond C2 compounds. This can only be achieved if complementary characterization techniques are used, relevant control materials are measured, and complete characterization datasets are discussed.

The second major direction we foresee is related to the reporting of electrocatalytic data to compare materials' performance. Besides FE, production rates and long-term stability and operation performance of the electrodes should be reported. Special attention must be paid to the normalization of the electrochemical parameters to allow a proper comparison and screening of porous carbon electrocatalysts. The control of the catalytic layer thickness when using gas diffusion electrodes, local pH and electrolyte concentrations should be carefully described.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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References

Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest

1. W. Zhang, Y. Hu, L. Ma, G. Zhu, Y. Wang, X. Xue, R. Chen, S. Yang, Z. Jin, Progress and Perspective of Electrocatalytic CO_2 Reduction for Renewable Carbonaceous Fuels and Chemicals, Adv. Sci. 5 (2018) 1700275. https://doi.org/10.1002/advs.201700275.

2. S. Jin, Z. Hao, K. Zhang, Z. Yan, J. Chen, Advances and Challenges for the Electrochemical Reduction of CO_2 to CO: From Fundamentals to Industrialization, Angew. Chemie. 133 (2021) 20795–20816. https://doi.org/10.1002/ange.202101818.

3. Q. Chen, P. Tsiakaras, P. Shen, Electrochemical Reduction of Carbon Dioxide: Recent Advances on Au-Based Nanocatalysts, Catalysts. 12 (2022) 1348. https://doi.org/10.3390/catal12111348.

4. J. Yu, J. Wang, Y. Ma, J. Zhou, Y. Wang, P. Lu, J. Yin, R. Ye, Z. Zhu, Z. Fan, Recent Progresses in Electrochemical Carbon Dioxide Reduction on Copper-Based Catalysts toward Multicarbon Products, Adv. Funct. Mater. 31 (2021) 2102151. https://doi.org/10.1002/adfm.202102151.

5. M. Usman, M. Humayun, M.D. Garba, L. Ullah, Z. Zeb, A. Helal, M.H. Suliman, B.Y. Alfaifi, N. Iqbal, M. Abdinejad, A.A. Tahir, H. Ullah, Electrochemical Reduction of CO_2: A Review of Cobalt based Catalysts for Carbon Dioxide Conversion to Fuels, Nanomaterials. 11 (2021) 2029. https://doi.org/10.3390/nano11082029.

6. A. Marcos-Madrazo, C. Casado-Coterillo, J. Iniesta, A. Irabien, Use of Chitosan as Copper Binder in the Continuous Electrochemical Reduction of CO_2 to Ethylene in Alkaline Medium, Membranes. 12 (2022) 783. https://doi.org/10.3390/membranes12080783.

7. X. Duan, J. Xu, Z. Wei, J. Ma, S. Guo, S. Wang, H. Liu, S. Dou, Metal-Free Carbon Materials for CO_2 Electrochemical Reduction, Adv. Mater. 29 (2017) 1701784. https://doi.org/10.1002/adma.201701784.

8. S. Ntakirutimana, W. Tan, M.A. Anderson, Y. Wang, Editors' Choice-Review-Activated Carbon Electrode Design: Engineering Trade-off with Respect to Capacitive Deionization Performance, J. Electrochem. Soc. 167 (2020) 143501. https://doi.org/10.1149/1945-7111/abbfd7.

9. L. Dai, Carbon-based metal-free catalysts: design and applications, John Wiley & Sons, 2018.

10. J. Iniesta, L. García-Cruz, A. Gomis-Berenguer, C.O. Ania, Carbon Materials based on Screen-Printing Electrochemical Platforms in Biosensing Applications, SPR Electrochem. 13 (2016) 133–169. https://doi.org/10.1039/9781782620273-00133.

11. Q. Abbas, M. Mirzaeian, A.A. Ogwu, M. Mazur, D. Gibson, Effect of Physical Activation/Surface Functional Groups on Wettability and Electrochemical Performance of Carbon/Activated Carbon Aerogels based Electrode Materials for Electrochemical Capacitors, Int. J. Hydrogen Energy. 45 (2020) 13586–13595. https://doi.org/10.1016/j.ijhydene.2018.04.099.

12. M. Sevilla, G.A. Ferrero, A.B. Fuertes, CO2 Storage on Nanoporous Carbons in, K. Kaneko, F. Rodriguez-Reinoso (Eds.), Nanoporous Materials for Gas Storage (2019) Springer, Green Energy and Technology series, pp 287. https://doi.org/10.1007/978-981-13-3504-4_11.

13. C. Li, Y. Wang, N. Xiao, H. Li, Y. Ji, Z. Guo, C. Liu, J. Qiu, Nitrogen-doped Porous Carbon from Coal for High Efficiency CO_2 Electrocatalytic Reduction, Carbon. 151 (2019) 46–52. https://doi.org/10.1016/j.carbon.2019.05.042.

14. X. Hao, X. An, A.M. Patil, P. Wang, X. Ma, X. Du, X. Hao, A. Abudula, G. Guan, Biomass-Derived N-Doped Carbon for Efficient Electrocatalytic CO_2 Reduction to CO and Zn-CO_2 Batteries, ACS Appl. Mater. Interfaces. 13 (2021) 3738–3747. https://doi.org/10.1021/acsami.0c13440.

15. A. H. Wang et al., Efficient Electrocatalytic Reduction of CO_2 by Nitrogen-Doped Nanoporous Carbon/Carbon Nanotube Membranes: A Step Towards the Electrochemical

CO₂ Refinery, Angew. Chem. Int. Ed. 56 (2017) 7847-7852. https://doi.org/10.1002/ange.201703720.

16. H. Wang, J. Jia, P. Song, Q. Wang, D. Li, S. Min, C. Qian, L. Wang, Y.F. Li, C. Ma, T. Wu, J. Yuan, M. Antonietti, G.A. Ozin, Efficient Electrocatalytic Reduction of CO₂ by Nitrogen-Doped Nanoporous Carbon/Carbon Nanotube Membranes: A Step Towards the Electrochemical CO₂ Refinery, Angew. Chem. 129 (2017) 7955–7960. https://doi.org/10.1002/ange.201703720.

17. J. Gui, K. Zhang, X. Zhan, Y. Yu, T. Huang, Y. Li, J. Xue, X. Jin, S. Gao, Y. Xie, Nitrogen-Doped Porous Carbon Nanosheets as a Robust Catalyst for Tunable CO₂ Electroreduction to syngas, Sustain. Energy Fuels. 6 (2022) 1512–1518. https://doi.org/10.1039/d1se02034j.

18. Y. Dong, Q. Zhang, Z. Tian, B. Li, W. Yan, S. Wang, K. Jiang, J. Su, C.W. Oloman, E.L. Gyenge, R. Ge, Z. Lu, X. Ji, L. Chen, Ammonia Thermal Treatment toward Topological Defects in Porous Carbon for Enhanced Carbon Dioxide Electroreduction, Adv. Mater. 32 (2020) 2001300. https://doi.org/10.1002/adma.202001300.

19. W. Li, M. Seredych, E. Rodríguez-Castellón, T.J. Bandosz, Metal-free Nanoporous Carbon as a Catalyst for Electrochemical Reduction of CO₂ to CO and CH₄, ChemSusChem. 9 (2016) 606–616. https://doi.org/10.1002/cssc.201501575.

(*) 20. S. Messias, M.N. da Ponte, A.S. Reis-Machado, Carbon Materials as Cathode Constituents for Electrochemical CO₂ Reduction, C. 5 (2019) 83. https://doi.org/10.3390/c5040083.

The electrocatalytic activity of various carbons (including carbon black, mesoporous carbons, carbon nanofibers, graphene and derivatives, carbon nanotubes) is described and comparatively discussed with the findings of theoretical computational studies.

21. G. Wang, M. Liu, J. Jia, H. Xu, B. Zhao, K. Lai, C. Tu, Z. Wen, Nitrogen and Sulfur Co-doped Carbon Nanosheets for Electrochemical Reduction of CO₂, ChemCatChem. 12 (2020) 2203–2208. https://doi.org/10.1002/cctc.201902326.

22. Y. Song, W. Chen, C. Zhao, S. Li, W. Wei, Y. Sun, Metal-Free Nitrogen-Doped Mesoporous Carbon for Electroreduction of CO₂ to Ethanol, Angew. Chemie - Int. Ed. 56 (2017) 10840–10844. https://doi.org/10.1002/anie.201706777.

23. W. Zhang, B. Jia, X. Liu, T. Ma, Surface and Interface Electrochemistry in Metal-Free Electrocatalysts for Electrochemical CO₂ Reduction, SmartMat. 3 (2022) 5–34. https://doi.org/10.1002/smm2.1090.

24. C. Jia, W. Ren, X. Chen, W. Yang, C. Zhao, (N, B) Dual Heteroatom-Doped Hierarchical Porous Carbon Framework for Efficient Electroreduction of Carbon Dioxide, ACS Sustain. Chem. Eng. 8 (2020) 6003-6010. https://doi.org/10.1021/acssuschemeng.0c00739.

25. M. Kuang, A. Guan, Z. Gu, P. Han, L. Qian, G. Zheng, Enhanced N-Doping in Mesoporous Carbon for Efficient Electrocatalytic CO₂ Conversion, Nano Res. 12 (2019) 2324–2329. https://doi.org/0.1007/s12274-019-2396-6.

(*) 26. D. Hursán, A.A. Samu, L. Janovák, K. Artyushkova, T. Asset, P. Atanassov, C. Janáky, Morphological Attributes Govern Carbon Dioxide Reduction on N-Doped Carbon Electrodes, Joule. 3 (2019) 1719–1733. https://doi.org/10.1016/j.joule.2019.05.007.

Correlations of the physicochemical properties of N-doped electrocatalysts with the electrocatalytic performance. A series of N-doped carbon materials are used, with varied mesoporosity and similar microporosity.

(*) 27. W. Liu, J. Qi, P. Bai, W. Zhang, L. Xu, Utilizing Spatial Confinement Effect of N Atoms in Micropores of Coal-based Metal-Free Material for Efficiently Electrochemical Reduction of Carbon Dioxide, Appl. Catal. B Environ. 272 (2020) 118974. https://doi.org/10.1016/j.apcatb.2020.118974.

Useful comparison of functionalized carbon materials with their corresponding un-functionalized control materials. The role of the micropores in CO2ER is nicely discussed.

28. W. Li, B. Herkt, M. Seredych, T.J. Bandosz, Pyridinic-N Groups and Ultramicropore Nanoreactors enhance CO_2 Electrochemical Reduction on Porous Carbon Catalysts, Appl. Catal. B Environ. 207 (2017) 195–206. https://doi.org/10.1016/j.apcatb.2017.02.023.

(*) 29. Y. Song, S. Wang, W. Chen, S. Li, G. Feng, W. Wei, Y. Sun, Enhanced Ethanol Production from CO_2 Electroreduction at Micropores in Nitrogen-Doped Mesoporous Carbon, ChemSusChem. 13 (2020) 293–297. https://doi.org/10.1002/cssc.201902833.

Successful demonstration of outstanding production rates of ethanol in N-doped carbon electrocatalysts with varied mesoporosity and similar N-doping. Interesting correlations with the average micropore size.

30. J. Wordsworth, T.M. Benedetti, A. Alinezhad, R.D. Tilley, M.A. Edwards, W. Schuhmann, J.J. Gooding, The Importance of Nanoscale Confinement to Electrocatalytic Performance, Chem. Sci. 11 (2020) 1233–1240. https://doi.org/10.1039/c9sc05611d.

31. F. Naseem, P. Lu, J. Zeng, Z. Lu, Y.H. Ng, H. Zhao, Y. Du, Z. Yin, Solid Nanoporosity Governs Catalytic CO_2 and N_2 Reduction, ACS Nano. 14 (2020) 7734–7759. https://doi.org/10.1021/acsnano.0c02731.

32. J. H. Bae, J.-H. Hanw, T. D. Chung, Electrochemistry at nanoporous interfaces: new opportunity for electrocatalysis Phys. Chem. Chem. Phys., 14 (2012) 448–463. https://doi.org/10.1039/c1cp22927c

33. H. Ma, Y.L. Ying, Recent progress on nanopore electrochemistry and advanced data processing, Curr. Opin. Electrochem. 26 (2021) 100675. https://doi.org/10.1016/j.coelec.2020.100675.

(*) 34. K. Fu, P.W. Bohn, Nanopore electrochemistry: A Nexus for Molecular Control of Electron Transfer Reactions, ACS Cent. Sci. 4 (2018) 20–29. https://doi.org/10.1021/acscentsci.7b00576.

This paper highlights the development of nanopore-confined electrochemistry, addressing concepts of electron transfer in nanopores, and providing an outlook for new approaches in nanopore electrochemistry.

35. M. Li, M.N. Idros, Y. Wu, T. Burdyny, S. Garg, X.S. Zhao, G. Wang, T.E. Rufford, The Role of Electrode Wettability in Electrochemical Reduction of Carbon Dioxide, J. Mater. Chem. A. 9 (2021) 19369–19409. https://doi.org/10.1039/d1ta03636j.

36. J. Xiong, Z. Zhu, W. Ye, L. Mu, X. Lu, J. Zhu, Regulating Surface Wettability and Charge Density of Porous Carbon Particles by in Situ Growth of Polyaniline for Constructing an Efficient Electrical Percolation Network in Flow-Electrode Capacitive Deionization, Langmuir. 38 (2022) 12263–12272. https://doi.org/10.1021/acs.langmuir.2c01885.

37. Q. Li, W. Zhu, J. Fu, H. Zhang, G. Wu, S. Sun, Controlled Assembly of Cu Nanoparticles on Pyridinic-N Rich Graphene for Electrochemical Reduction of CO_2 to ethylene, Nano Energy. 24 (2016) 1–9. https://doi.org/10.1016/j.nanoen.2016.03.024.

38. M. Seredych, J. Jagiello, T.J. Bandosz, Complexity of CO_2 Adsorption on Nanoporous Sulfur-Doped Carbons - Is Surface Chemistry an Important Factor?, Carbon . 74 (2014) 207–217. https://doi.org/10.1016/j.carbon.2014.03.024.

39. T. Liu, S. Ali, Z. Lian, C. Si, D. S. Su, B. Li, Phosphorus-doped onion-like carbon for CO_2 electrochemical reduction: the decisive role of the bonding configuration of phosphorus, J. Mater. Chem. A, 6 (2018) 19998-20004. https://doi.org/10.1039/C8TA06649C

40. P. Yao, Y. Qiu, T. Zhang, P. Su, X. Li, H. Zhang, N-Doped Nanoporous Carbon from Biomass as a Highly Efficient Electrocatalyst for the CO_2 Reduction Reaction, ACS Sustain. Chem. Eng. 7 (2019) 5249–5255. https://doi.org/10.1021/acssuschemeng.8b06160.

41. J. Wang, I. Senkovska, M. Oschatz, M.R. Lohe, L. Borchardt, A. Heerwig, Q. Liu, S. Kaskel, Highly Porous Nitrogen-Doped Polyimine-based Carbons with Adjustable Microstructures for CO_2 Capture, J. Mater. Chem. A. 1 (2013) 10951–10961. https://doi.org/10.1039/c3ta11995e.

42. S. Reljic, M. Martinez-Escandell, J. Silvestre-Albero, Effect of Porosity and Surface Chemistry on CO_2 and CH_4 Adsorption in S-Doped and S-/O-co-Doped Porous Carbons, C. 8 (2022) 41. https://doi.org/10.3390/c8030041.

43 Á. Sánchez-Sánchez, F. Suárez-García, A. Martínez-Alonso, J.M.D. Tascón, Influence of Porous Texture and Surface Chemistry on the CO_2 Adsorption Capacity of Porous Carbons: Acidic and Basic Site Interactions, ACS Appl. Mater. Interfaces. 6 (2014) 21237–21247. https://doi.org/10.1021/am506176e.

44. P.A.S. Moura, E. Vilarrasa-Garcia, D.A.S. Maia, M. Bastos-Neto, C.O. Ania, J.B. Parra, D.C.S. Azevedo, Assessing the Potential of Nanoporous Carbon Adsorbents from Polyethylene Terephthalate (PET) to Separate CO_2 from Flue Gas, Adsorption. 24 (2018) 279–291. https://doi.org/10.1007/s10450-018-9943-4.

45. M.C. Gutiérrez, D. Carriazo, C.O. Ania, J.B. Parra, M.L. Ferrer, F. Del Monte, Deep Eutectic Solvents as both Precursors and Structure Directing Agents in the Synthesis of Nitrogen Doped Hierarchical Carbons Highly Suitable for CO_2 Capture, Energy Environ. Sci. 4 (2011) 3535–3544. https://doi.org/10.1039/c1ee01463c.

46. J. Patiño, M.C. Gutiérrez, D. Carriazo, C.O. Ania, J.B. Parra, M.L. Ferrer, F. Del Monte, Deep Eutectic Assisted Synthesis of Carbon Adsorbents Highly Suitable for Low-Pressure Separation of CO_2-CH_4 Gas Mixtures, Energy Environ. Sci. 5 (2012) 8699–8707. https://doi.org/10.1039/c2ee22029f.

47. C.O. Ania, E. Raymundo-Piñero. Nanoporous carbons with tuned porosity, in K. Kaneko, F. Rodriguez-Reinoso (Eds.), Nanoporous Materials for Gas Storage (2019) Springer, Green Energy and Technology series, pp 403.

(*) 48. W. Zheng, D. Wang, Y. Zhang, S. Zheng, B. Yang, Z. Li, R.D. Rodriguez, T. Zhang, L. Lei, S. Yao, Y. Hou, Promoting Industrial-level CO_2 Electroreduction Kinetics via Accelerating Proton Feeding on a Metal-Free Aerogel Electrocatalyst, Nano Energy. 105 (2023) 107980. https://doi.org/10.1016/j.nanoen.2022.107980.

Demonstration of the scalability of carbon electrocatalysts for the electrochemical reduction of CO_2 using a gas diffusion electrode.

49. Y. Zhang, X. Wang, S. Zheng, B. Yang, Z. Li, J. Lu, Q. Zhang, N. M. Adli, L. Lei, G. Wu, Y. Hou, Hierarchical Cross-Linked Carbon Aerogels with Transition Metal-Nitrogen Sites for Highly Efficient Industrial-Level CO2 Electroreduction, Adv. Funct. Mater. 2021, 31, 2104377-10.

50. Y. Guo, F. Pan, W. Chen, Z. Ding, D. Yang, B. Li, P. Ming, C. Zhan, The Controllable Design of Catalyst Inks to Enhance PEMFC Performance: A Review, Electrochemical Energy Reviews 4 (2021) 67-100. https://doi.org/10.1007/s41918-020-00083-2

51. A.M. Limaye, J.S. Zeng, A.P. Willard, K. Manthiram, Bayesian Data Analysis reveals no Preference for Cardinal Tafel Slopes in CO_2 Reduction Electrocatalysis, Nat. Comm. 12 (2021) 703. https://doi.org/10.1038/s41467-021-20924-y.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: