Phosphate-Tolerant Oxygen Reduction Catalysts
Qing Li,† Gang Wu,*† David A. Cullen,‡ Karren L. More,# Nathan H. Mack,§ Hoon T. Chung,† and Piotr Zelenay*†

†Materials Physics and Applications Division and #Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States
‡Materials Science and Technology Division and §Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

ABSTRACT: Increased oxygen reduction reaction (ORR) kinetics, improved CO tolerance, and more efficient water and heat management represent significant advantages that high-temperature polymer electrolyte fuel cells (HT-PEFCs) operating with a phosphoric acid-doped polybenzimidazole (PBI) membrane offer over traditional Nafion-based, low-temperature PEFCs. However, before such HT-PEFCs become viable, the detrimental effect of phosphate chemisorption on the performance of state-of-the-art Pt-based cathode catalysts needs to be addressed. In this study, we propose a solution to the severe poisoning of Pt-based PEFC cathode catalysts with phosphates (H₂PO₄⁻ and HPO₄²⁻) by replacing standard Pt/C catalysts with phosphate-tolerant, nonprecious metal catalyst (NPMC) formulations. Catalysts with a very high surface area (845 m² g⁻¹) were synthesized in this work from polyaniline (PANI), iron, and carbon using a high-temperature approach. The effects of metal precursors and metal loading on the morphology, structure, and ORR activity of the NPMCs were systematically studied. Electrochemical measurements indicated that as-prepared Fe-based catalysts (PANI-Fe-C) can tolerate phosphate ions at high concentrations and deliver ORR performance in 5.0 M H₃PO₄ that is superior to that of Pt/C catalysts. A 30 wt % Fe-derived catalyst was found to have the most porous morphology and the highest surface area among studied Fe-based catalysts, which correlates with the highest ORR activity of that catalyst. These cost-effective and well-performing ORR catalysts can potentially replace Pt/C catalysts in phosphoric acid-based HT-PEFCs.

KEYWORDS: oxygen reduction, nonprecious metal catalysis, phosphate tolerance, Pt poisoning, phosphoric acid fuel cells

1. INTRODUCTION
Among the various fuel cell technologies under development today, the high-temperature polymer electrolyte fuel cell (HT-PEFC), operating with a polybenzimidazole (PBI) membrane in the presence of polyphosphoric acid, offers several potential advantages over fuel cells that utilize proton-conducting, low-temperature Nafion membranes. Performance losses due to water flooding in the cathode are a key issue in traditional low-temperature fuel cells. In that context, the operating temperature of a PBI-based HT-PEFC is typically between 150 and 200 °C, preventing the formation of liquid water in the cathode. In addition, hydrogen produced from reformed hydrocarbons is contaminated with low levels of carbon monoxide (CO), which negatively impacts fuel cell performance by poisoning the Pt catalysts. The poisoning effect strongly depends on temperature and becomes much less pronounced at elevated temperatures. Li et al. reported that above 185 °C, phosphoric acid fuel cells (PAFCs) can tolerate up to 3% CO, i.e., carbon monoxide levels present in hydrogen from reforming of hydrocarbons, thus eliminating the need for subsequent CO removal.

PEFCs operating with Nafion or other perfluorosulfonic-acid membranes rely on liquid water for proton conductivity. This limits their operating temperature to ca. 100 °C, above which such membranes dehydrate and their conductivity drops sharply. H₃PO₄-doped PBI membranes can operate at temperatures above 160 °C and without the need for humidification, reaching a protonic conductivity similar to that of Nafion at 80 °C and 95% relative humidity. Other potential benefits of H₃PO₄-doped PBI fuel cells include enhanced kinetics of both electrode reactions at elevated temperatures, the ease of stack assembly with phosphoric acid-saturated polymer membranes, and release of high-quality heat.
The state-of-the-art cathode catalysts for HT-PEFCs are presently based on Pt. However, the oxygen reduction reaction (ORR) activity of Pt-based catalysts is significantly impaired in the presence of $\text{H}_3\text{PO}_4$ due to the severe Pt catalyst poisoning by chemisorbed dihydrogen phosphate ($\text{H}_3\text{PO}_4^-$) and hydrogen phosphate ($\text{HPO}_4^{2-}$) ions. One possible way of dealing with cathode poisoning by phosphate ions is to replace the Pt catalyst with nonprecious metal catalysts (NPMCs). In addition to the obvious cost advantage, they are generally more tolerant to surface-active phosphates. It is worth noting that in addition to the obvious cost advantage, NPMCs are especially suitable for HT-PEFC applications. Finally, the most active NPMCs today contain ca. 90% carbon, which is susceptible to corrosion at high potentials of the cathode via a reaction with water: $\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4e^- \quad (E^\circ = 0.207 \, \text{V})$. The liquid-water-free environment is expected to help the overall durability of NPMCs by significantly lowering water activity. To date, the ORR on NPMCs in phosphoric acid media has been largely unexplored, particularly in terms of the ORR mechanism and synthesis–structure–activity correlations in such media.

The effect of metal precursors and metal loading on the ORR activity and durability of polyaniline (PANI)-derived Fe-based NPMCs are systematically discussed below. To the best of our knowledge, this is the first comprehensive report on the implementation of NPMCs as ORR catalysts in phosphoric acid electrolytes.

2. EXPERIMENTAL SECTION

2.1. Catalyst Synthesis. Ketjenblack EC 300J (KJ-300J) was used as the carbon support in the catalyst synthesis. It was first treated in HCl solution for 24 h to remove metal impurities, followed by a HNO₃ treatment to introduce oxygen-containing functionalities onto the carbon surfaces. In a typical approach, 2.0 mL of aniline was then dispersed in a 1.0 M HCl solution. The suspension was kept below 10 °C, while 5.0 g of oxidant (ammonium peroxydisulfate, APS) and metal precursors (0.7, 2.3, 9.1 g of FeCl₃ or 15.8 g of Co(NO₃)₂·6H₂O) were added. Then 0.4 g of the acid-treated carbon support was mixed with the above PANI suspension. After constant mixing for 24 h to allow aniline to polymerize, get unstable and inactive species from the catalyst, followed by a thorough wash with deionized water. Finally, the catalyst was heat-treated again at 900 °C in nitrogen for 3 h. The final product was labeled as PANI-M-C (M: Fe or Co, C: KJ). In order to explore the role of nitrogen and transition metals in the ORR catalysis, the PANI-coated carbon, denoted as PANI-C, was subject to the same heating and chemical post-treatments in a controlled experiment.

2.2. Electrochemical Characterization. The ORR activity and four-electron selectivity in the presence of $\text{H}_3\text{PO}_4$ were evaluated using rotating ring electrode (RDE) and rotating ring-disk electrode (RRDE). The electrochemical tests were carried out using a CHI Electrochemical Station (Model 750b) in a conventional three-electrode cell at a room temperature. A graphite rod and an Ag/AgCl electrode in 3.0 M NaCl were used as the counter and reference electrodes, respectively. The catalyst loading was 0.6 mg cm$^{-2}$. Performance of the reference Pt catalyst was evaluated using a 20 wt % E-TEK Pt/C catalyst at two loadings: 20 and 60 $\mu g$ cm$^{-2}$. The steady-state ORR polarization plots were recorded in an O₂-saturated electrolyte using a potential step of 0.03 V and wait-period of 30 s at each RDE potential. The disk rotation rate was varied between 400 to 2500 rpm. The effect of phosphates on ORR activity was measured in a 0.1 M HClO₄ solution at various concentrations of $\text{H}_3\text{PO}_4$. In RRDE experiments, the ring potential was set to 1.2 V. Before experiments, the Pt catalyst in the ring was activated by potential cycling in 0.1 M HClO₄ from 0 to 1.4 V at a scan rate of 50 mV s$^{-1}$ for 10 min. The catalyst selectivity for four-electron reduction of O₂ was calculated from the H₂O₂ yield using the following equation:

$$\text{H}_2\text{O}_2(\%) = 200 \times \frac{I_R/N}{(I_R/N) + I_D}$$

Here, $I_D$ and $I_R$ are the disk current and ring current, respectively, and $N$ is the ring collection efficiency (36% in this work).

2.3. Physical Characterization. The surface area of catalysts was measured by nitrogen adsorption at 77 K using Brunauer–Emmett–Teller (BET) analysis on a Quantachrome Autosorb iQ-c instrument. Each sample was degassed by heating at 150 °C under vacuum prior to measuring the surface area. The metal content in Fe-based catalysts was determined by thermogravimetric analysis (TGA) using a TA Q50 instrument under flowing dry air. Raman spectra were obtained using a Kaiser Holospec Raman system at 514 nm excitation. The sample morphology was characterized by scanning electron microscopy (SEM) on a Hitachi S-5400. The crystallinity of samples was determined by X-ray diffraction (XRD) performed on an automated Rigaku diffractometer equipped with a Cu Kα radiation source and a graphite monochromator operating at 45 kV and 40 mA. The diffraction patterns were acquired at a scan rate of 1.2° min$^{-1}$ with a step of 0.02°.

X-ray photoelectron spectrometry (XPS) was performed on an ESCA 210 and MICROLAB 310D spectrometer. The high-resolution spectra were acquired in normal emission geometry with a conventional Mg X-ray source at a pass energy of 20 eV. Transmission electron microscopy (TEM) and STEM images from the same particles were acquired using a Hitachi HF3300 TEM operated at an accelerating voltage of 300 kV. Atomically resolved aberration-corrected annular dark-field (ADF) scanning transmission electron microscopy (STEM) images were recorded using a Nion UltraSTEM-100 operated at 60 kV. Specimens were mounted on lacy carbon films using a standard drop-cast method. For inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis, the carbon component was first removed by dry-ashing the catalysts in air at 700 °C. The ash residue was then digested in a heated mixture of trace-metal-grade concentrated hydrochloric and nitric acids, and the resultant solution was diluted with water. The iron concentrations in the product solutions were measured using a PerkinElmer Optima 3300 DV ICP-OES to calculate the mass fraction of iron in the powder samples.
studied in this work were heat-treated at 900°C. NPMCs work, iron and cobalt salts were selected as precursors for electron selectivity. The steady-state ORR polarization and temperature that provided the highest ORR activity and four-electron selectivity. The steady-state ORR polarization and H2O2-yield plots, obtained with three different NPMCs in 5.0 M H3PO4 at a disk rotation rate of 900 rpm, are shown in Figure 1a. The reason for the use of a high concentration of phosphoric acid fuel cells. Of the three tested NPMCs, PANI-Fe-C gave the most positive ORR onset potential (0.92 V vs RHE) and half-wave potential (0.77 V vs RHE). The latter ORR half-wave potential value is by ca. 40 mV lower than that measured previously in 0.5 M H2SO4 (0.81 V). The metal-free PANI-C catalyst showed relatively poor ORR activity, attesting to the key role of the transition metal in inducing ORR activity of NPMCs. These results are in good agreement with our previous data obtained in sulfuric acid electrolyte. The four-electron selectivity was found to correlate well with the ORR activity of the catalysts. The lowest H2O2 yield, below 1% at all studied potentials, was obtained for the PANI-Fe-C catalyst. The H2O2 yield of PANI-C was ca. 2%. Low H2O2 yields in the presence of H2PO4 corroborated high selectivity of the catalysts for the four-electron reduction of O2 to H2O rather than the two-electron reduction to H2O.

The kinetic current density, extracted from the Koutecký–Levich plots, was used to generate Tafel plots in Figure 1b. Theoretically, a Tafel slope (b) of 120 mV dec−1 is due to the rate-determining step associated with the first electron transfer. A Tafel slope of 60 mV dec−1 has been linked to the effect of surface oxides or adsorbed oxygen intermediates on ORR kinetics, governed by the Temkin adsorption isotherm, according to which the activation energy of an electrochemical process becomes dependent on the surface concentration of intermediates at high surface coverage values. The Tafel slope values measured with the PANI-Co-C (b = 104 mV dec−1) and metal-free catalyst (b = 126 mV dec−1) are close to 120 mV dec−1, suggesting that the first electron transfer may be rate determining. The lower Tafel slope observed with PANI-Fe-C (b = 93 mV dec−1) points to the possible effect of surface diffusion of the ORR intermediates. It is worth noting that the Tafel slope values measured with PANI-Fe-C in 5.0 M H3PO4 and 0.5 M H2SO4 are similar, 93 and 87 mV/dec, respectively, suggesting a very similar or the same ORR reaction mechanism in both electrolytes. Since the Tafel slope and onset potential values for PANI-Fe-C and PANI-Co-C catalysts are different, the ORR reaction mechanism and active sites are likely different, too. This is supported by the large difference in the onset ORR potentials for the two catalysts by as much as 90 mV (Figure 1a).

The ORR activity and four-electron selectivity of the PANI-Fe-C catalyst in 5.0 M phosphoric acid were also studied as a function of initial Fe loadings between 3 and 30 wt% (Figure 2a). A significant improvement in the ORR was found with a catalyst synthesized using 10 wt% of Fe, relative to the catalyst obtained using 3 wt% of Fe. An increase in the ORR current was observed in the mass-transfer region and, however, small, in the kinetic region when the Fe content in the synthesis was raised to 30 wt%. PANI-Fe-C synthesized using 30 wt% of Fe generated the least amount of H2O2 — below 1% — a very low value for a nonprecious metal ORR catalyst. The observed ORR activity correlated well with the BET surface area of the PANI-Fe-C catalysts. The electrochemical surface area (S_e) values for three PANI-Fe-C samples (Figure 2b) were calculated from the double layer capacitance determined by cyclic voltammetry, using 0.2 F cm−2 (20 μF cm−2) as the unit capacitance of carbon-based catalysts. This is the value used before for glassy carbon. While this approach is not exact it represents a good S_e estimate.

In the same trend as BET surface area data, the 30 wt% Fe-derived catalyst reveals the highest electrochemical surface area of 235 m2 g−1, compared to 97 m2 g−1 and 59 m2 g−1, measured with 10 and 3 wt% Fe samples, respectively. It is worth noting that the BET surface area, measured by N2 adsorption from a gas phase, includes the area of micropores (<2.0 nm). In turn, S_e the effective electrochemical surface area, represents only that fraction of the BET area that is accessible to the electrolyte.
Sₐ is predominantly associated with mesopores (>2 nm) and macropores (>50 nm).³⁶,³⁷ This is the reason why Sₐ for high surface-area catalysts is always smaller than the BET surface area. At the same time, the reaction mechanism was found to be independent of the Fe content, as suggested by similar Tafel slope values, which were all in the range from 90 to 97 mV dec⁻¹ (Figure 2c).

The number of electrons involved in the ORR at different potentials using the best performing 30 wt % Fe-derived PANI-Fe-C catalyst was calculated from the Koutecky–Levich plots (Figure 3). As shown in Figure 3b, the Koutecky–Levich plots at 0.49 and 0.37 V overlap and are also parallel to the plots recorded at 0.61 and 0.70 V, indicating that the number of electrons transferred in the ORR remains constant in the studied potential range. The n values of 3.63–3.93 (with a mean value of 3.78), calculated from the slope of the Koutecky–Levich plots in Figure 3b, are slightly lower than the n values of 3.98–3.99 obtained from RRDE data in Figure 2a. This difference likely results from the high sensitivity of the slope and intercept values of the Koutecky–Levich lines to any scatter in the experimental data. The high values of n attest to either a direct four-electron or a two-plus-two-electron mechanism of oxygen reduction on the studied NPMCs in concentrated H₃PO₄.

3.2. Catalyst Morphology. To learn more about the origin of ORR activity of PANI-Fe-C catalysts, the physical and chemical properties the catalysts were studied as a function of Fe loading used in the synthesis. The bulk Fe content and BET surface area of three PANI-Fe-C catalysts are shown in Table 1. While, surprisingly, the Fe content in the catalyst synthesized using 30 wt % Fe is the lowest (~2 wt %), the BET surface area of that catalyst is the highest, 845 m² g⁻¹ (a high value for a KJ-supported NPMC).²⁴ Noteworthy, while the nominal metal content of Co used for synthesizing the PANI-Co-C catalyst was 30 wt % the Co content in the final catalyst was 8 wt %. In good agreement with the BET surface-area values, SEM images in Figure 4 attest to a significantly more porous structure for
the 30 wt % Fe-derived catalyst than for the 3 and 10 wt % Fe-derived catalysts.

The distinct XRD peaks in Figure 4 (shown by red star) for 3 and 10 wt % Fe-derived catalysts can be assigned to FeS ($2\theta = 17.1^\circ$, $18.7^\circ$, $29.9^\circ$, $31.9^\circ$, $33.7^\circ$, $35.7^\circ$, $43.3^\circ$, $47.2^\circ$, $54.0^\circ$, $63.5^\circ$, and $70.8^\circ$). The sulfide originates from the use of APS as oxidant for aniline polymerization during the catalyst synthesis (see Experimental Section for details). Of note is the lack of FeS peaks in the XRD spectrum from the 30 wt % Fe-derived catalyst, which only contains carbon peaks at ca. $25^\circ$ and $44^\circ$. In contrast to the 3 and 10 wt % Fe-derived catalysts, in situ formed FeS in the 30 wt % Fe-derived catalyst is more efficiently leached out during the acid treatment step. The fact that the highest initial Fe loading used in the synthesis leads to the lowest bulk Fe content in the final product as well as the highest BET surface area may indicate that the in situ formed FeS acts as an effective sacrificial pore-forming agent during acid leaching. More research is required to understand why the FeS formed with 30 wt % of Fe is not protected by carbon layers.

Advanced TEM and STEM were performed to study the 30 wt % Fe PANI-Fe-C catalyst to provide additional insight regarding the structure of the newly developed catalysts with high surface area. As shown in Figure 5a, the predominant morphology consisted of an intimate mixture of agglomerated KJ particles and rumpled, multilayered graphene sheets. Fe particles, most likely FeS, were also occasionally identified (yellow arrow, Figure 5a). An SEM image (Figure 5b) of the same region shown in the TEM image in Figure 5a also indicates that the rumpled, sheet-like morphology of the multilayered graphene envelopes the KJ particles. In Figure 5c, an ADF-STEM image of a multilayered graphene sheet and associated EELS analysis indicates that single Fe atoms are dispersed across the surface of the graphene. These Fe atoms were highly mobile under the electron beam, indicating that Fe is not incorporated within the carbon lattice. Additionally, EELS identified nitrogen in thicker areas of the layered graphene sheets.

At this point, one can only speculate on the unique graphene morphology of the carbon observed in 30 wt % Fe-derived catalysts. Larger FeS nanoparticles in 3 and 10 wt % Fe-derived catalysts appear to be locked within agglomerated carbon particles, while smaller FeS particles in the 30 wt % Fe-derived catalyst are enveloped in thin sheets of graphene and thus exposed. The carbon morphology in 3 and 10 wt % Fe-derived catalysts is clearly more agglomerated and sphere-like, rather than layer- or sheet-like. The formation of graphene sheets is a direct result of the initial higher Fe-content; the fact that most of it disappears during acid leaching is also a direct result of the formation of the graphene sheets. The XPS analysis of the three PANI-Fe-C catalysts supports the hypothesis of the FeS leaching by revealing that Fe and S content near the catalyst surface decreases with an increase in the Fe loading used in the synthesis (Table 2). It is worth noting that a decrease in the total nitrogen content is observed with an increase in the amount of Fe precursor without an associated drop in ORR activity. This suggests that ORR activity of these NPMCs does not depend on the total nitrogen doping but, more likely, on the location and bonding of the nitrogen atoms within the carbon/graphene lattice. Relative to the two catalysts with lower initial Fe loadings, the high-resolution N 1s peak for the 30 wt % Fe-derived catalyst shows that the relative amount of graphitic nitrogen increases with the Fe loading, leading to an

Table 1. Fe Content and BET Surface Area of PANI-Fe-C Catalysts

<table>
<thead>
<tr>
<th>Fe loading in synthesis (nominal, wt %)</th>
<th>Fe content in final catalysts (by ICP and TGA, wt %)</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3%</td>
<td>10%</td>
<td>148</td>
</tr>
<tr>
<td>10%</td>
<td>12%</td>
<td>292</td>
</tr>
<tr>
<td>30%</td>
<td>2%</td>
<td>845</td>
</tr>
</tbody>
</table>

Figure 4. SEM images (top) and XRD patterns (bottom) for PANI-Fe-C catalysts as a function of Fe loading used during the synthesis.
enhancement in the ORR activity in H₃PO₄ and implying that graphitic nitrogen can significantly impact catalyst activity.

3.3. ORR Performance of NPMCs vs Pt/C Catalysts.

The effect of H₃PO₄ on the ORR activity of the 30 wt % Fe-derived catalyst compared with a Pt/C reference catalyst was studied in O₂-saturated 0.1 M HClO₄ solution as a function of H₃PO₄ concentration (Figure 6). The ORR activity of the 30 wt % Fe-derived catalyst is nearly independent of H₃PO₄ concentration (Figure 6a), as is the double layer capacitance in N₂-saturated 0.1 M HClO₄ solution (Figure 6b). A gradual drop in the limiting current in the electrolyte with increasing H₃PO₄ concentration (Figure 6a) is caused by lower values of the diffusion coefficient and O₂ solubility as well as a higher value of the kinematic viscosity of H₃PO₄ relative to 0.1 M HClO₄ solution (effectively water). They all lead to a decrease in the mass-transfer-limited current of oxygen oxidation. These results are very different from those obtained with a Pt/C reference catalyst, which exhibit a loss in the ORR activity by as much as ca. 60 mV at E₁/₂ in 0.3 M H₃PO₄ (Figure 6c). Cyclic voltammetry (Figure 6d) indicates that the number of Pt sites for hydrogen adsorption decreases with an increase in phosphoric acid concentration as a result of phosphate adsorption, an observation that is in good agreement with previous results. The potential of Pt-surface oxidation shifts positively in the presence of phosphates, confirming the formation of a strong chemical bond between the phosphate ions and Pt atoms.

ORR polarization plots recorded with the 30 wt % Fe-derived catalyst and the reference Pt/C catalyst at two Pt loadings of 20 µgPt cm⁻² and 60 µgPt cm⁻² in 5.0 M H₃PO₄ are shown in Figure 7. The NPMC performance trails that of the Pt/C reference catalyst, but only when the high Pt loading of 60 µgPt cm⁻² is used. The NPMC clearly outperforms the Pt/C reference at a “standard” RDE loading of 20 µgPt cm⁻², often viewed as representative for fuel cell cathode applications. The higher value of limiting current density for the NPMC has been linked to the greater thickness of the NPMC layer. It should be pointed out that all electrochemical measurements in this work were carried out at a room temperature. The experiments focusing on the effect of temperature on performance of a fuel cell with a PBI-type membrane at 150 °C, and possibly at higher temperatures, are planned. We hope to report results of this study in the near future, together with the data on the optimization of the NPMC cathode.

4. CONCLUSIONS

The ORR activity of Pt/C is significantly reduced in H₃PO₄-based electrolytes due to severe poisoning of the catalyst.
surface by chemisorbed H$_2$PO$_4$$^-$ and HPO$_4^{2-}$ ions. In this study, PANI-Fe-C catalysts for oxygen reduction, derived from polyaniline, transition metal, and carbon, were studied in phosphoric acid electrolytes. These NMPCs showed much improved phosphate tolerance compared to their Pt/C counterparts. The use of a high Fe loading in the PANI-Fe-C catalyst synthesis (30 wt %) resulted in a final catalyst with an extremely low Fe content but high surface area (845 m$^2$ g$^{-1}$) and enhanced ORR activity, likely due to the formation of a unique carbon morphology (sheet-like multilayered graphene), which also results in improved acid leaching of the FeS. Although the catalyst obtained using the higher Fe loading has relatively low nitrogen content, its activity is higher than that of the two other Fe-based catalysts, indicating that ORR performance of NPMCs depends more on how nitrogen is incorporated into the carbon/graphene lattice rather than on the total nitrogen content. RRDE experiments and kinetic analysis attest to a four-electron selectivity of nonprecious metal ORR catalysts in H$_3$PO$_4$ electrolytes. Further understanding of the factors governing the ORR activity of nonprecious metal catalysts in the presence of phosphates as well as their implementation into a PBI-based HT-PEFCs will be the focus of our future research.

■ AUTHOR INFORMATION

Corresponding Authors
* E-mail: wugang@lanl.gov (G.W.).
* E-mail: zelenay@lanl.gov (P.Z.).

Notes
The authors declare no competing financial interest.

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