The role of palladium in a hydrogen economy

We are facing accelerated global warming due to the accumulation of greenhouse gases. A hydrogen-based economy is one potential approach toward maintaining our standard of living while lowering carbon dioxide emissions. Palladium is a unique material with a strong affinity to hydrogen owing to both its catalytic and hydrogen absorbing properties. Palladium has the potential to play a major role in virtually every aspect of the envisioned hydrogen economy, including hydrogen purification, storage, detection, and fuel cells. Major aspects of current research and potential applications of palladium-based nanomaterials in various hydrogen technologies are presented in this review.

Brian D. Adams and Aicheng Chen*

Department of Chemistry, Lakehead University, 955 Oliver Road, Thunder Bay, ON P7B 5E1, Canada *E-mail: achen@lakeheadu.ca

Global society has become strongly dependent on the excessive use of fossil fuels1. Oil, coal, and natural gas have been utilized extensively to power automobiles, plants, and factories, causing a dramatic build-up of greenhouse gases in the atmosphere2. Unlike fossil fuels, the combustion of hydrogen does not generate carbon dioxide (CO2), but only water vapor. The ultimate goals of a hydrogen-based economy include the production of hydrogen while generating minimal greenhouse gases, the development of efficient infrastructures for hydrogen storage and transport, and the harnessing of its energy via fuel cells3.

Palladium (Pd) exhibits a number of exceptional properties which enable its application in a myriad of hydrogen technologies. Palladium has the ability to absorb large volumetric quantities of hydrogen at room temperature and atmospheric pressure, and subsequently forms palladium hydride (PdH_x). As shown in Fig. 1, the absorbed hydrogen atoms occupy interstitial octahedral sites of the facecentered cubic lattice⁴. The temperatures and equilibrium pressures required for the formation of various metal hydrides are compared in Table 15. Palladium can form a hydride under ambient conditions and the formed PdH_x exhibit the noble character of Pd⁶. This attractive

Table 1 Metal hydrides and their hydrogen storage properties.

Metal	Hydride	wt.% H	P _{eq} , T
Pd	PdH _{0.6}	0.56	0.02 bar, 298 K
Mg	MgH ₂	7.60	1 bar, 573 K
LaNi ₅	LaNi ₅ H ₆	1.37	2 bar, 298 K
ZrV ₂	$ZrV_2H_{5.5}$	3.01	10 ⁻⁸ bar, 323 K
FeTi	FeTiH ₂	1.89	5 bar, 303 K
Mg ₂ Ni	Mg_2NiH_4	3.59	1 bar, 555 K
TiV ₂	TiV_2H_4	2.60	10 bar, 313 K

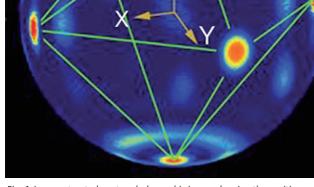


Fig. 1 A reconstructed neutron holographic image showing the positions of six Pd atoms surrounding a hydrogen nucleus in an octahedral interstitial site of an fcc lattice. Reprinted with permission from⁴. © 2004 American Institute of Physics.

Table 2 Key properties of PdH_x.

Property	Value	Reference	
Lattice Constant (nm at 298 K)			
Pd	0.3890	15	
PdH _{0.015} (α _{max})	0.3894	15	
PdH _{0.607} (β _{min})	0.4025	15	
Volumetric Expansion (α/β-phase, %)	10.4	15	
Diffusion Coefficient (cm ² .s ⁻¹ at 298 K)			
α -phase	3.8×10^{-7}	15	
β-phase	2.0×10^{-7}	16	
ΔH _{plat} (kJ/mol H at 298 K)	19.1 ± 0.2	16	
ΔS _{plat} (J/K.mol H)	46.6	14	

hydrogen absorbing property has undergone extensive study in both the gas phase⁷⁻⁹ and under electrochemical conditions¹⁰⁻¹³. There are several classical, informative reviews, and other literature available in regard to PdH_x, which discuss the physical, thermodynamic, and kinetic properties of the system¹⁴⁻²¹. Some of the key properties of PdH_x are

Molecular H₂ dissociation is the first step in absorption toward the formation of metal hydrides. Other than Pd, most metals require energy input in order to overcome an activation barrier, which necessitates the application of high hydrogen pressures or elevated

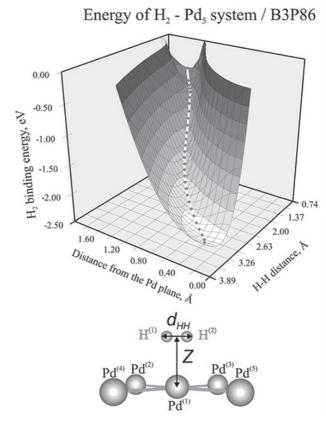


Fig. 2 Potential energy surface for a H_2 molecule bound to the planar Pd_5 cluster. The H₂ dissociation path on the potential surface is indicated by the thick line with crosses. The calculations were performed by the DFT/ B3P86 method. Reprinted with permission from²³. © 2004 Plenum Publishing Corporation.

temperatures. On palladium surfaces, the dissociative adsorption of H₂ molecules occurs with little or no activation energy barrier^{22,23}. Fig. 2 shows the activation-less pathway of H₂ dissociation on a Pd₅ cluster. The superior dissociative properties of Pd enable it to serve as a catalyst to facilitate hydrogen absorption and desorption in other metal hydrides²⁴. Further, its inherent selectivity for hydrogen, fast sorption kinetics, and reversibility of hydride formation allow Pd-based alloy membranes to attain a high hydrogen gas quality at 99.99999 % purity. Hydrogen sensors are also being investigated that draw on the changes in the properties of Pd upon exposure to hydrogen²⁵.

Carbon-supported Pt is commonly used as an electrocatalyst in low temperature fuel cells that utilize hydrogen or small organic molecule feedstocks²⁶. The high cost of Pt and the limited world supply are barriers to widespread use^{27,28}. Pd is of great interest as a substitute material for Pt, not only due to its chemical similarity to Pt, but also because of its significantly reduced cost (approximately 1/5 that of Pt) and 50 fold greater abundance²⁶. The extensive use of Pd for hydrogen storage remains impractical, however, due to its relatively high price. Nevertheless, with the application of appropriate cost-saving methods such as alloying with less expensive metals and utilizing nanoscale

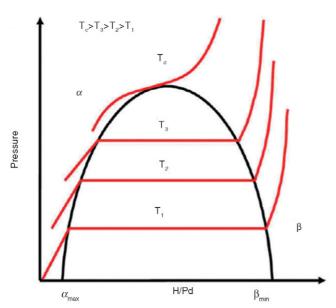


Fig. 3 Phase diagram for PdH_x. Reprinted with permission from⁶. © 2009 Elsevier.

materials, palladium has the potential to play a significant role in many aspects of the hydrogen economy, from purifying hydrogen to harnessing its energy via fuel cells. In this review, the utilization of Pd as a material for applications in several hydrogen technologies is examined. The current state of research and implications regarding the next steps in the development of such materials are also discussed.

Hydrogen purification

Hydrogen may be produced from either hydrocarbons or water by employing a wide array of techniques. The most environmentally friendly production technique involves the electrolysis of water, which uses off-peak power or power from renewable sources such as wind turbines or solar cells. Unfortunately, \sim 70 % of the electricity in the US is generated through combustion of coal and natural gas. Currently, the majority of H₂ is produced in the form of *syngas* that is generated by the gasification of hydrocarbons, which generates large amounts of CO and CO₂.

A high purity hydrogen gas stream is crucial to the performance of fuel cells since certain species poison the catalysts even at very low concentrations²⁹. In the case of CO, a strong adsorbing species, less than 10 ppm is typically required³⁰. The application of a highly selective palladium-based membrane may be utilized to purify the gas, and is currently the most advanced method of doing so³⁰. A major drawback for membranes that are comprised of pure Pd is hydrogen embritlement³¹. The absorption of hydrogen into Pd occurs in two distinct phases. The α -phase appears at low concentrations of hydrogen (solid solution), and the β -phase forms at high concentrations of hydrogen (metal hydride). A schematic phase diagram for PdH_x is displayed in Fig. 3.

Associated with the α/β -phase transition is an expansion of the face-centered cubic crystal lattice. This large expansion of the lattice, due to hydrogen embrittlement, can cause the cracking of the membrane. In general, β_{min} decreases and α_{max} increases in conjunction with elevated temperature. As a result, the width of the co-existence region or miscibility gap (β_{min} - α_{max}) decreases with rising temperatures until a critical threshold $T_c = 570$ K (bulk Pd) is reached. Above T_c , the miscibility gap is no longer observed. For this reason, membranes that are comprised of pure Pd are held above 570 K in order to avoid hydrogen embrittlement⁶.

It has been shown that the size of the Pd particles has an effect on this phase transition³². The miscibility gap and T_c are decreased with the use of nanoparticles^{33,34}. A comparison of the hydrogen absorption isotherms for Pd bulk and Pd nanoparticles is illustrated in Fig. 4. The

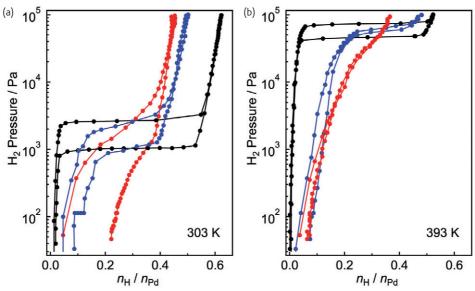


Fig. 4 Hydrogen absorption isotherms for Pd bulk (black) and Pd nanoparticles of size 7.0 ± 0.4 nm in diameter (blue) and 2.6 ± 0.4 nm in diameter (red). Reprinted from³³. © 2009 Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

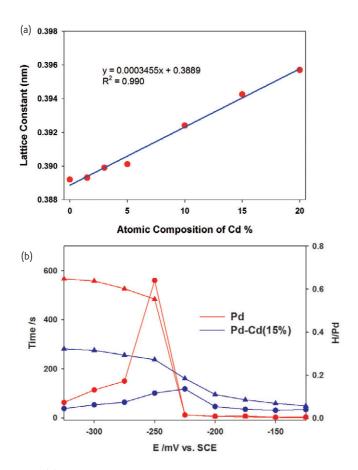


Fig. 5 (a) Vegard's plot showing the dependence of the fcc lattice constant on the normalized atomic composition of Cd in Pd-Cd alloys (b) and an overlay showing the H/(Pd+Cd) ratio (triangles) and time to reach steady state hydrogen sorption (circles) versus potential for the Pd and Pd-Cd(15%) electrodes. Reprinted with permission from 38,39. ©2009, 2010 American Chemical Society.

hysteresis in the PC isotherm of Pd nanoparticles (2.6 \pm 0.4 nm in diameter) disappeared at 393 K. The absence of hysteresis, in addition to the absence of a plateau region in the equilibrium pressure, implies that the critical state of the $\alpha\text{-}$ and $\beta\text{-}$ phases has been attained. Thus, a remarkable decrease in T_c was recognized in Pd nanoparticles 19 .

Hydrogen embrittlement may also be controlled at ambient temperatures by alloying Pd with metals which have larger atoms than Pd itself. In PdAg, for example, which is the most common hydrogen extraction metal alloy used by industry³⁵, the lattice is pre-expanded by the silver atoms and thus is less influenced by hydrogen than a pure Pd lattice³⁶. An optimal hydrogen permeation value is achieved at a silver content of 23 wt.%³⁵. The isotherms for PdAg alloys do not show a well-defined plateau as in the case of Pd, and the lattice expands continuously in this region. The α/β -phase transition results in a volumetric expansion of only 0.38 % for this alloy³⁷. The same effect has been seen with Pd-Cd nanostructures. A composition of Pd-Cd (15 at.%) was found to eliminate the α/β -phase transition with optimal hydrogen solubility and, consequently, increased the

kinetics of the absorption process³⁸. The lattice constant relationship for the Pd-Cd alloys along with the potential dependence of hydrogen electrosorption is shown in Fig. 5³⁹.

In heterogeneous catalysis, it is observed that poisons (e.g., sulphur, arsenic, and carbon monoxide) deactivate catalyzed reactions through irreversible adsorption at active sites⁴⁰. Recently, palladium-based sorbents were shown to effectively remove the contaminants mercury, arsenic, selenium, and phosphorus from high temperature syngas⁴¹⁻⁴³. There is a competition between the poison and the reactant for available adsorption sites at the catalyst surface. In the case of Pd-based hydrogen selective membranes, poisoning species tend to inhibit the dissociative adsorption of hydrogen at the surface, which is the initial step in the absorption/desorption process. Pd is especially vulnerable to hydrogen sulphide (H₂S) and carbon monoxide (CO), which are among the contaminant species that are present in the hydrocarbon fuels used for hydrogen production^{30,44}. The alloying of Pd with Cu has been reported to offer a significant tolerance to H₂S in the hydrogen gas stream when a PdCu membrane is operated at high temperatures (> 908 K)44,45. On the other hand, both Pd and PdCu membranes suffer greatly from the effects of H₂S at lower temperatures, forming Pd₄S and Pd-Cu-S layers, respectively, which nullify hydrogen dissociation or permeation⁴⁶.

Electrochemical hydrogen absorption experiments with Pd electrodes in the presence of CO have revealed that the adsorption of CO strongly blocks the capacity for hydrogen insertion as well as its removal from the metal 47,48 . The hydrogen permeance of $Pd_{0.75}Ag_{0.25}$ membranes has also been measured in the presence of pure H_2 or mixtures of H_2 with CO and H_2O at various temperatures 49 . A strong access inhibition by CO, owing to the robust interaction between CO and Pd was observed; however, the effect was eliminated at temperatures higher than 623 K. Much of the work done with respect to the poisoning species of Pd-based hydrogen permeable membranes has suggested that conducting hydrogen purification at elevated temperatures is likely to decrease the problematic effects described above.

Hydrogen storage

Hydrogen storage and transportation are among the most challenging issues to overcome, as they are critical prerequisites to the realization of a hydrogen-based economy. There are three primary classes of material that are currently under study for hydrogen storage in automotive applications: organic chemical hydrides, metal hydrides, and carbon materials for physisorption⁵⁰. In 2002, the US Department of Energy set quantitative goals for the hydrogen content of storage devices (6 wt.% by 2010, then 9 wt.% by 2015). These targets have not been met, and consequently, the DOE has revised the target to 5.5 wt.% by 2015⁵¹. The critical properties that a hydrogen storage material should possess include that it be (i) lightweight, (ii) inexpensive and readily available, (iii) accommodating for high

REVIEW The role of palladium in a hydrogen economy

volumetric and gravimetric densities of hydrogen, and exhibit (iv) rapid sorption kinetics, (v) easy activation, (vi) low temperature dissociation or decomposition, (vii) appropriate thermodynamic properties, (viii) long-term cycling stability, and (ix) high reversibility⁵². Palladium should not be considered as a sole hydrogen storage material since it is somewhat expensive and has a low gravimetric hydrogen density⁵³. However, it does satisfy all of the other requirements that define a hydrogen storage material, which enable it to "assist" in the hydrogenation and dehydrogenation of other materials.

Palladium acts not only as a catalyst to facilitate the uptake and dissociation of hydrogen in other metal hydrides 54 , it can also protect the surface from corrosion, allowing for the study of air-sensitive samples in ambient conditions $^{55-57}$. At temperatures of below 250 K, hydrogen absorption and desorption is effectively hindered and it becomes frozen within the sample. This allows for the absorption of a desired hydrogen concentration at room temperature, followed by rapid cooling to cryogenic temperatures to facilitate analysis of the sample. A capping layer of 2-5 nm is typically sufficient for this purpose 55 .

Inexpensive, lightweight, and high capacity metal hydrides such as MgH₂ (7.6 wt.%), are considered as viable candidates for practical hydrogen storage applications⁵⁸⁻⁶⁰. There are, however, two major issues inherent to MgH₂: (i) the sorption kinetics involved are quite sluggish; and (ii) MgH2 has a high thermodynamic stability requiring temperatures that exceed 300 °C for the desorption of hydrogen^{58,61,62}. Although hydrogenation is most commonly carried out in a high-pressure hydrogen atmosphere at elevated temperatures, metals such as Pd and its alloys may be electrochemically charged with hydrogen at ambient temperatures 10-13,63-68. In contrast, magnesium and its alloys may not be charged via this method as they dissolve in acidic solutions or form magnesium hydroxide in alkaline media⁶⁹. However, these issues can be resolved through the use of a Pd capping layer^{61,70,71}. Vermeulen et al. ⁷² have shown that a film of Mg_xTi_{1-x} that is capped with a thin (3 - 4 nm) layer of Pd can be electrochemically charged with hydrogen. The cumulative hydrogen storage capacity of this material has been shown to approach 1750 mAh/g, which corresponds to 6.4 wt.%. Neissen et al. 73 have also obtained this capacity using Pd-capped Mg-Sc alloys.

Even though many metals absorb hydrogen exothermally, it is necessary to overcome a certain activation energy barrier, which is contingent on surface elements, in order to dissociate hydrogen molecules 55 . Since many metals have slow hydrogenation kinetics, Pd can be employed as a catalyst to dissociate hydrogen molecules, and thus decrease the hydrogenation time 62 . The activation energies of $\rm H_2$ sorption for bulk MgH $_2$, mechanically milled MgH $_2$, and nanocatalyst-doped MgH $_2$, are shown in Fig. $\rm 6^{52}$. The activation barrier is drastically lowered via nanocatalyst doping. In addition, the collision frequency between H $_2$ molecules and transition metal nanoparticles may increase with the reduction in the size of the catalyst.

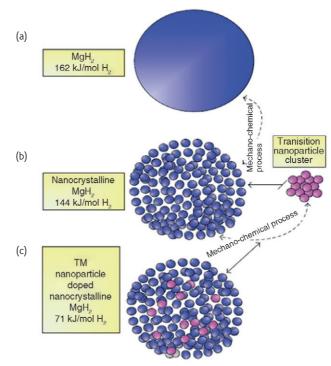


Fig. 6 Conceptual model of MgH_2 cluster (a) plain, (b) nanocrystalline, and (c) nanocatalyst-doped materials. Reprinted with permission from 52 . © 2008 Hindawi Publishing Corporation.

Fig. 7 displays the kinetics of hydrogen absorption to Mg with different particle sizes (a) and to Pd-doped Mg nanoparticles (b). Pure Mg takes three times as long to attain the equivalent hydrogen capacity as Pd-doped Mg⁷⁴. A computational study has revealed that an optimal hydrogenation catalyst would not only have superior dissociation capabilities, but also exhibit low potency dissociated hydrogen atom binding with the metal³⁶. Pd offers an attractive compromise for these properties, which may be further enhanced when it is alloyed with other metals.

Another promising class of hydrogen storage material is carbon⁷⁵. Carbon offers the advantages of being lightweight and inexpensive, while exhibiting onboard reversibility and rapid sorption kinetics. In contrast to the chemisorption in metal hydrides⁷⁶, the phenomenon of physical adsorption is essentially the accumulation of undissociated hydrogen molecules upon a surface of microporous carbon. It has been found that hydrogen uptake in carbon is proportional to its inherent surface area and/or pore volume. High hydrogen adsorption capacities (3 – 8 wt.%) may be obtained only at very low cryogenic temperatures or high pressures^{77,78}. Operating within the cryogenic domain poses certain challenges such as maintaining the storage vessel at low temperatures⁷⁹. The storage of hydrogen using carbon materials at practical temperatures relies on a chemical reaction between carbon and hydrogen atoms, which involves the cleavage of the H₂ molecule. This may be accomplished through the use of transition metal catalysts80.

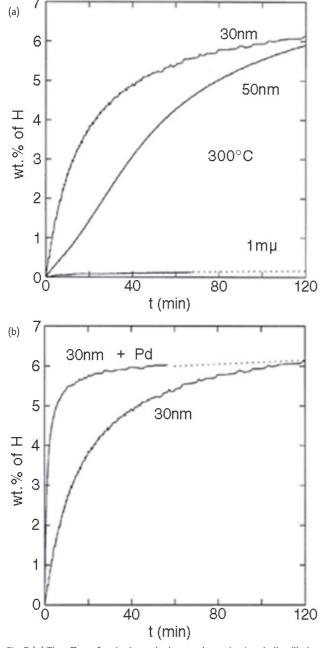


Fig. 7 (a) The effect of grain size on hydrogen absorption into ball-milled Mq, and (b) a comparison of nanosized Mq with and without a Pd catalyst. Reprinted with permission from⁷⁴. © 1999 Elsevier.

The metallic doping of carbon materials results in the following phenomena, which are collectively termed as the hydrogen spillover mechanism: (i) H₂ molecules dissociate on the metal catalyst particles; (ii) H atoms migrate from the metal catalyst particles to the carbon substrate material; and (iii) H atoms diffuse on the substrate^{81,82}. The hydrogen spillover mechanism is illustrated in Fig. 8. When spillover occurs, the hydrogen capacity of the combined system (carbon + metal) will typically exceed that of the individual components⁸³. An advantage

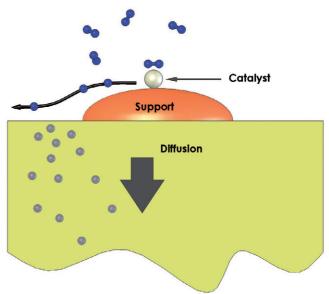


Fig. 8 Spillover mechanism: (i) dissociative adsorption of H₂ molecules on a metal catalyst, (ii) migration of H atoms to the support, and (iii) diffusion on the bulk of the carbon material. Reprinted from⁸². © 2007 Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

that is provided by the use of Pd as the catalyst is that a portion of the hydrogen is stored within the catalyst itself (as PdH_v). Hence, the capacity of the overall material is likely to be higher than that of a nonabsorbing metal.

Recent DFT calculations have shown that the migration of atomic hydrogen from a metal nanoparticle to a graphitic substrate is kinetically and thermodynamically inefficient and limits the rate of H spillover84,85. Experimental studies have also shown that a further enhancement of the storage capacity of metal-doped carbons might be achieved by chemically modifying the carbon substrate via the introduction of oxygen functionalities⁸⁶⁻⁸⁸. Some work has been done to examine the effects of an introduced catalyst. However, as mentioned above, a catalyst that exhibits an excellent compromise between hydrogen dissociation and migration from the metal should produce much better results. Because the strength of the C-H interaction tends to be much lower than that of the Pd-H, alloying Pd with metals which have a lower affinity for hydrogen should enhance the effects of spillover. This was recently validated when PdCd nanoparticles, which were dispersed on activated carbon, generated a spillover enhancement that was far greater than the Pd nanoparticles alone, due to the weak strength of the Cd-H bonds of surface resident Cd atoms⁸⁹.

Hydrogen detection

Various types of sensor have been studied and implemented for the sensing of oxidizing and reducing gases⁹⁰. Recently, H₂ sensors have gained great interest due to the undesired and/or unanticipated presence of hydrogen within certain commercial/industrial environments. Although hydrogen is attractive as a carbon-free fuel, it is colorless, odorless, an asphyxiant (through displacement of oxygen), and it is highly flammable in air²⁵. A potential hydrogen gas sensor must satisfy four requirements for wide-scale deployment, namely: sensitivity, selectivity, specificity, and cost. Most approaches utilize Pd as a catalyst, since Pd has a great absorptive affinity for H₂. The mechanical, electrical, magnetic, and optical properties of the metal undergo dramatic changes on exposure to hydrogen⁵⁵.

There are two primary classes of hydrogen selective sensors that are based on Pd. The most popular of these exploits the increased electrical resistivity of Pd, which is built up due to the intensified electron scattering that is initiated by the incorporation of hydrogen^{25,91,92}. The alternate class is an optical sensor that consists of a layer of Pd, which is coated onto an optically active material that translates the concentration of hydrogen into an optical signal^{93,94}. The key principle that underlies hydrogen sensing is the conversion of the α -phase (conductive) of Pd to the β -phase (less conductive). Cleverly, the nanoeffect on the α/β -phase transition has been utilized advantageously in many cases. Yang et al. 95 discovered that Pd nanowires have the capacity for detecting H2 much more rapidly than Pd films. Favier et al. 96 elucidated a less conventional mechanism for enabling hydrogen switches and sensors, which was based on palladium mesowire arrays. Rather than the observation of an increase in resistivity upon exposure to hydrogen, they noted a decrease. This mechanism involves the closing of nanoscopic gaps within the nanowires, which are caused by the dilation of the palladium grains as they undergo hydrogen absorption. Hydrogen spillover has also been observed in the work of Kolmakov et al. 97 from Pd catalyst nanoparticles to SnO₂ nanowire/ nanobelt gas sensors.

Fuel cell catalysis

Pt is the most commonly employed electrocatalyst in low temperature fuel cells²⁶. The disadvantages of Pt include its high cost, limited world supply, and vulnerability to CO which is present in the H₂ feed stream or is produced as an intermediate during the oxidation of small organic molecules^{27,98}. In addition, although Pt exhibits the highest activity among pure metals in cathodic oxygen reduction reactions, it is still not a satisfactory candidate for conducting this sluggish reaction on its own. Numerous studies have been undertaken toward the identification of alternative catalyst materials that might replace Pt, either partially or completely. Pt-based alloys such as Pt-Ru⁹⁹ and Pt-Pb¹⁰⁰ are not only less expensive; they also exhibit enhanced oxidative activity relative to Pt. Although Pd is of great interest as a substitute material for Pt, it does not appear to be active enough for utilization as a catalyst in most oxidation or reduction reactions. Hence, Pd alloys and composites thereof have been widely investigated for these purposes. Pd-Pt bimetallic catalysts have been found to outperform Pt in many reactions, and Pd is shown to be a far superior catalyst than Pt in formic acid oxidation. For the oxygen reduction reaction, Pd-alloys have also demonstrated improved performance when compared to Pt,

especially in the presence of methanol. The transition from Pt-based to Pd-based catalysts has commenced and will likely result in the development of more cost effective materials with enhanced activity toward the commercialization of fuel cells.

Conclusions and research outlook

This review has described the significant roles of Pd-based nanomaterials in hydrogen purification, storage, detection, and fuel cells. It is anticipated that Pd-based nanomaterials will be vital to both enable and develop a hydrogen economy. The extent of the application of these nanomaterials will be largely contingent on cost and availability. Critical targets in Pd-based nanomaterials research should therefore be three-fold: (i) to advance our understanding to a point where it will be possible to successfully tailor high-performance Pd-based nanomaterials by design; (ii) to develop novel synthesis methods that allow precise control over product morphology and composition and which will serve to optimize the catalytic and hydrogen absorbing efficiencies of Pd-based nanomaterials; and (iii) to design and fabricate robust nano-scale palladium entities that can survive under the difficult conditions of high temperatures and various oxidizing or reducing environments.

In regard to hydrogen absorbing applications (e.g., purification, storage, and detection), there are two common, albeit detrimental issues that should be encompassed within the research focus; specifically, the development of countermeasures to negate both the onset of hydrogen embrittlement and the effects of poisoning species. Hydrogen solubility plays an essential kinetic role in certain applications (e.g., storage, fuel cell catalysts) that exploit hydrogen dissociation, where surface interactions are of greater concern than those involved with bulk phase absorption. In these cases, the adsorption strength is a crucial factor. While research on hydrogen storage materials has slowed somewhat, due to discouraging results combined with failures to meet stipulated requirements, it is now more imperative than ever to investigate the use of Pd-based catalysts to assist in the realization of this goal. Combinatory studies, including both experimental and computational methods, to facilitate further elucidation of the dynamics of the alloying effect should help us to reach a deeper understanding of the electronic and geometric nuances that are at play in this process. Intensive research has been recently conducted on the metal hydrides for improving adsorption/desorption properties for hydrogen storage. The development of more advanced computational techniques for the detailed study of hydride formation and the desorption of hydrogen may be a beneficial avenue of research that will serve to support experimental work and/or lead to a better understanding of bimetallic or trimetallic Pd-based hydride systems. In conclusion, the issues of cost, hydrogen embrittlement, poisoning species, hydrogen solubility, and hydrogen adsorption strength are critical areas for investigative research toward the development of functional Pd-based nanomaterials to enable technologies that will drive the hydrogen economy.

Acknowledgements

This work was supported by a Discovery Grant from the Natural Sciences and Engineering Research Council of Canada (NSERC). A.C. acknowledges NSERC and the Canada Foundation of Innovation (CFI) for the Canada Research Chair Award in Material and Environmental Chemistry.

REFERENCES

- 1. Chen, P., and Zhu, M., Mater Today (2008) 11, 36.
- 2. van den Berg, A. W. C., and Areán, C. O., Chem Commun (2008) 668.
- 3. Chen, A., and Holt-Hindle, P., Chem Rev (2010) 110, 3767.
- 4. Cser, L., et al., Appl Phys Lett (2004) 85, 1149.
- 5. Schlapbach, L., and Züttel, A., Nature (2001) 414, 353.
- 6. Narehood, D. G., et al., Int J Hydrogen Energ (2009), 34, 952.
- 7. Kishore, S., et al., J Alloy Compd (2005) 389, 234.
- 8. Yamauchi, M., et al., J Phys Chem C (2008) 112, 3294.
- 9. Kobayashi, H., et al., J Am Chem Soc (2008) 130, 1828.
- 10. Gabrielli, C., et al., J Electrochem Soc (2004) 151, A1925.
- 11. Gabrielli, C., et al., J Electrochem Soc (2004) 151, A1937.
- 12. Losiewicz, B., et al., J Electroanal Chem (2007) 611, 26.
- 13. Duncan, H., and Lasia, A., Electrochim Acta (2008) 53, 6845.
- 14. Flanagan, T. B., and Oates, W. A., J Alloy Compd (2005) 404-406, 16.
- 15. Flanagan, T. B., and Oates, W. A., *Annu Rev Mater Sci* (1991) **21**, 269.
- 16. Knapton, A. G., Platinum Metals Rev (1977) 21, 44.
- 17. Lewis, F. A., *The Palladium Hydrogen System*, Academic Press Inc., London-New York, (1967).
- 18. Alefeld, G., et al., (eds.), Hydrogen in Metals I, Basic Properties, Springer-Verlag, Berlin-Heidelberg-New York, (1978).
- 19. Alefeld, G., et al., (eds.), Hydrogen in Metals II, Application-Oriented Properties, Springer-Verlag, Berlin-Heidelberg-New York, (1978).
- 20. Lewis, F. A., Int J Hydrogen Energ (1995) 20, 587.
- 21. Conrad, H., et al., Surf Sci (1974) 41, 435.
- 22. Nakatsuji, H., and Hada, M., J Am Chem Soc (1985) 107, 8264.
- 23. Bartczak, W. M., and Stawowska, J., Struct Chem (2004) 15, 447.
- 24. Zaluski, L., et al., J Alloy Compd (1995) 217, 295.
- 25. Şennik, E., et al., J Appl Phys (2010) 108, 054317.
- 26. Antolini, E., Energy Environ Sci (2009) 2, 915.
- 27. Sealy, C., Mater Today (2008) 11, 65.
- 28. Service, R. F., Science (2007) 315, 172.
- 29. Mejdell, A. L., et al., Sep Purif Technol (2009) 68, 178.
- 30. Park, E. D., et al., Catal Today (2009) 139, 280.
- 31. Li, H., et al., J Membrane Sci (2008) 324, 44.
- 32. Delogu, F., J Phys Chem C (2010) 114, 18085.
- 33. Yamauchi, M., et al., ChemPhysChem (2009) 10, 2566.
- 34. Eastman, J. A., et al., Phys Rev B (1993) 48, 84.
- 35. Sun, Y., et al., J Am Chem Soc (2004) 126, 5940.
- 36. Foletto, E. L., et al., Lat Am Appl Res (2008) 38, 79.
- 37. Axelrod, S. D., and Makrides, A. C., J Phys Chem (1964) 68, 2154.
- 38. Adams, B. D., et al., Langmuir (2010) 26, 7632.
- 39. Adams, B. D., et al., J Am Chem Soc (2009) 131, 6930.
- 40. Han, J.-N., et al., J Electrochem Soc (1997) 144, 4266.
- 41. Baltrus, J. P., et al., Fuel (2011) 90, 1992.
- 42. Baltrus, J. P., et al., Fuel (2010) 89, 1323
- 43. Granite, E. J., et al., Ind Eng Chem Res (2006) 45, 4844.
- 44. Miller, J. B., et al., J Phys Chem C (2009) 113, 18800.
- 45. Morreale, B. D., et al., | Membr Sci (2004) 241, 219.
- 46. O'Brien, C. P., et al., / Membr Sci (2010) 349, 380.
- 47. Czerwiński, A., J Electroanal Chem (1994) 379, 487.
- 48. Czerwiński, A., et al., J Electroanal Chem (1991) 304, 233.

- 49. Nguyen, T. H., et al., Chem Eng J (2009) 155, 55.
- 50. Sakintuna, B., et al., Int J Hydrogen Energ (2007) 32, 1121.
- 51. Schlapbach, L., Nature (2009) 460, 809.
- 52. Niemann, M. U., et al., / Nanomater (2008) 2008, 950967.
- 53. Grochala, W., and Edwards, P. P., Chem Rev (2004) 104, 1283.
- 54. Williams, M., et al., Int | Energy Res (2009) 33, 1171.
- 55. Remhof, A., and Borgschulte, A., ChemPhysChem (2008) 9, 2440.
- 56. Yamada, Y., et al., J Appl Phys (2010) 107, 043517.
- 57. Richardson, T. J., et al., Appl Phys Lett (2001) 78, 3047.
- 58. Pozzo, M., and Alfè, D., Int | Hydrogen Energ (2009) 34, 1922.
- 59. Shao, H., et al., J Alloy Comp (2008) 465, 527.
- 60. Gross, A. F., et al., Nanotechnology (2009) 20, 204005.
- 61. Friedrichs, O., et al., J Alloy Comp (2008) 463, 539.
- 62. Tang, F., et al., Nanotechnology (2008) 19, 465706.
- 63. Grdeń, M., et al., J Electroanal Chem (1999) 460, 30.
- 64. Czerwiński, A., et al., J Electroanal Chem (1999) 471, 190.
- 65. Grdeń, M., et al., J Electroanal Chem (2002) 532, 35.
- 66. Chen, S., et al., Electrochim Acta (2010) 56, 61.
- 67. Żurowski, A., et al., Electrochim Acta (2008) 53, 7812.
- 68. Łukaszewski, M., and Czerwiński, A., J Solid State Electrochem (2008) 12, 1589.
- 69. Juškėnas, R., et al., J Alloy Compd (2009) 467, 524.
- 70. Ma, T., et al., J Alloy Comp (2005) 391, 313.
- 71.Xiao, X., et al., Electrochem Commun (2009) 11, 515.
- 72. Vermeulen, P., et al., Electrochem Commun (2006) 8, 27.
- 73. Neissen, R. A. H., and Notten, P. H. L., J Alloy Compd (2005) 404, 457.
- 74. Zaluska, A., et al., J Alloy Compd (1999) 288, 217.
- 75. Dillon, A. C., et al., Nature (1997) 386, 377.
- 76. Contescu, C. I., et al., J Phys Chem C (2009) 113, 5886.
- 77. Wang, H., et al., J Am Chem Soc (2009) 131, 7016.
- 78. Liu, C., et al., Science (1999) 286, 1127.
- 79. Ahluwalia, R. K., and Peng, J. K., Int J Hydrogen Energ (2009) 34, 5476.
- 80. Tsao, C.-S., et al., J Phys Chem Lett (2010) 1, 1060.
- 81. Chen, L., et al., J Phys Chem C (2007) 111, 18995.
- 82. Bérubé, V., et al., Int J Energy Res (2007) 31, 637.
- 83. Zacharia, R., et al., Chem Phys Lett (2005) 412, 369.
- 84. Psofogiannakis, G. M., and Froudakis, G. E., J Phys Chem C (2009) 113, 14908.
- 85. Psofogiannakis, G. M., and Froudakis, G. E., J Am Chem Soc (2009) 131, 15133.
- 86. Wang, J., et al., Ind Eng Chem Res (2009) 48, 2920.
- 87. Yang, F. H., et al., J Phys Chem B (2006) 110, 6236.
- 88. Lueking, A. D., and Yang, R. T., Appl Catal A-Gen (2004) 265, 259.
- 89. Adams, B. D., et al., J Phys Chem C (2010) 114, 19875.
- 90. Joshi, R. K., et al., Nanoscale Res Lett (2009) 4, 1191.
- 91. Lee, E., et al., Int J Hydrogen Energ (2010) 35, 6984.
- 92. Huges, R. C., et al., J Electrochem Soc (1995) 142, 249.
- 93. Nazarpour, S., et al., Thin Solid Films (2010) 518, 5715. 94. Yang, M., et al., Sensor Actuat B-Chem (2010) 149, 161.
- 95. Yang, F., et al., ACS Nano (2010) 4, 5233.
- 96. Favier, F., et al., Science (2001) 293, 2227. 97. Kolmakov, A., et al., Nano Lett (2005) 5, 667.
- 98. Li, X., and Hsing, I.-M., Electrochim Acta (2006) 51, 3477.
- 99. Spinacé, E. V., et al., J Power Sources (2004) 129, 121.
- 100. Wang, J., et al., Chem Mater (2009) 21, 1716.